For the ester (1) this is 1.453 (2) Å, compared with a value of 1.458 (2) Å for the same ester lacking the 2-fluorine atom. If the F has a bond-shortening effect, it is very small in this case. For the phosphate triester (2) the C—OP bond length is 1.463 (2) Å. Here no direct comparison is available: an estimate made by interpolation between the values for the parent carboxylic and mesylate esters is 1.466 Å and is unlikely to be far out; and the conclusion is the same as for the carboxylic ester – if there is a bond-shortening effect of β-F it is very small.

For the sulfonate ester (3), on the other hand, there does appear to be significant effect. Of course one cannot reach more than provisional conclusions from the data for a single compound, however accurate they may be; but the C—OS bond length of 1.466 (3) Å is shorter than that for the parent mesylate [1.485 (9) Å (Jones, Kirby & Parker, 1992*a*)], and significantly so when compared with our preferred value for simple cyclohexyl sulfonate esters [1.483 (4) Å (Jones, Kirby & Parker, 1992*a*)]. So a provisional conclusion is that the introduction of a *gauche* β-fluorine atom does cause significant shortening of the equatorial cyclohexyl C—O*X* bond in sulfonate esters, compounds with a very good leaving group, and thus a particularly long bond. A similar effect is not ruled out for other systems, but it must be much smaller. In the following papers we look for more evidence for this effect in related systems.

We thank the Fonds der Chemischen Industrie for support. The crystallographic work on (1) and (3) was carried out in Göttingen, at the Institut für Anorganische Chemie der Universität.

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Bond Length and Reactivity. The Effect of β-Fluorine. Structures of the 4-Phenylbenzoate and Methanesulfonate Esters of *trans,cis*-4-*tert*-Butyl-2-fluorocyclohexanol

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Abstract. (1*SR*,2*RS*,4*SR*)-4-*tert*-Butyl-2-fluorocyclohexyl 4-phenylbenzoate, (1), $C_{23}H_{27}FO_2$, M_r = 354.47, triclinic, $P\bar{1}$, a = 7.559 (2), b = 9.869 (2), c = 14.347 (4) Å, α = 103.17 (2), β = 92.80 (2), γ = 104.33 (2)°, V = 1003.4 Å^3, Z = 2, D_x = 1.173 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.07 mm^{-1}, F(000) = 380, T = 293 K. Final R = 0.045 for 2500 unique observed reflections. (1*SR*,2*RS*,4*SR*)-4-*tert*-Butyl-2-fluorocyclohexyl methanesulfonate, (2), $C_{11}H_{21}FO_3S$, M_r = 252.35, monoclinic, $P2_1/c$, a = 17.090 (4), b = 7.678 (2), c = 10.806 (3) Å, β = 106.54 (2)°, V = 1359.2 Å^3, Z = 4, D_x = 1.233 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.23 mm^{-1}, F(000) = 544, T = 293 K. Final R =

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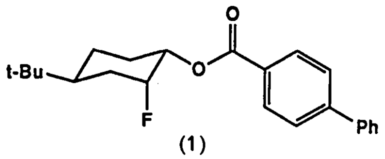
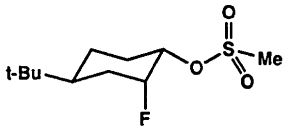
0.042 for 1641 unique observed reflections. The two structures have their ester substituents equatorial, and C—F axial, and thus *gauche* to the C—O*X* bond. F shows positional disorder in both compounds: this appears to be a characteristic of axial fluorine. The C—O*X* bond lengths are the same, within experimental error, as those in the corresponding compounds with fluorine equatorial [Jones, Kirby & Parker (1992). *Acta Cryst.* C**48**, 852–855]. The introduction of the 2-fluorine atom is associated with a significant shortening of the C—O bond in the sulfonate ester.

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*. We have established standard C—O*X* bond lengths in simple cyclohexanol derivatives (Jones, Kirby & Parker, 1992*b*,*c*,*d*), and in the previous paper in this series (Jones, Kirby & Parker, 1992*a*) we reported the structures of three esters – the 4-phenylbenzoate, the diphenyl phosphate and the 2-naphthalenesulfonate – of *trans*-2-fluorocyclohexanol. The introduction of the 2-fluorine substituent has little or no effect on the length of the C—O*X* bond in the two former cases, but a possibly significant shortening is observed for the sulfonate. We report here structures for two esters – the 4-phenylbenzoate (1) and the methanesulfonate (2) of the isomeric *cis*-2-fluorocyclohexanol – which have the F atom axial, rather than equatorial on the ring, but still *gauche* to the C—O*X* bond.

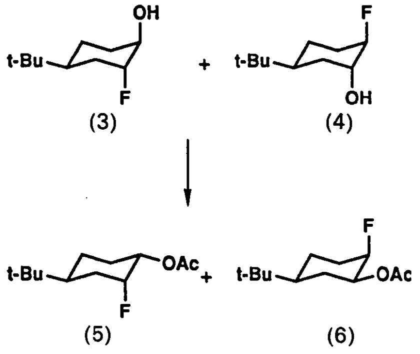


(1)



(2)

Experimental. *trans*,*cis*-4-*tert*-Butyl-2-fluorocyclohexanol was prepared with *cis*,*cis*-5-*tert*-butyl-2-fluorocyclohexanol, as a mixture of isomers, by a somewhat laborious sequence of reactions, starting from the mixed epoxides of 4-*tert*-butylcyclohexene described previously (Jones, Kirby & Parker, 1992*b*). These were opened with HF–pyridine, according to Olah & Meidar (1978), to give the two diaxial fluoroalcohols [(3) and (4), 86%], which were themselves converted under Mitsonobu (1981) conditions to the epimeric alcohols, as the acetate esters [(5) and (6)]. The esters were hydrolysed to the mixture of alcohols, which was used for the preparation of derivatives (Parker, 1989). No useful crystals of the diphenyl phosphate ester could be obtained.



trans,*cis*-4-*tert*-Butyl-2-fluorocyclohexyl 4-phenylbenzoate (1) was prepared from the mixture of alcohols by the method described previously for the parent ester (Jones, Kirby & Parker, 1992*b*). The products were separated by HPLC (eluant 2:1 CH_2Cl_2–hexane), to give the desired ester [(1), R_T 19.5 min] as prisms, m.p. 398.5–400 K. Single crystals were obtained as colourless tablets by vapour diffusion of hexane into a solution in CH_2Cl_2.

trans,*cis*-4-*tert*-Butyl-2-fluorocyclohexylmethanesulfonate (2). The mixture of mesylates, prepared as a yellow oil by the general method already described (Jones, Kirby & Parker, 1992*d*), was purified by flash column chromatography (eluant 3:2 hexane–diethyl ether). Recrystallization from CH_2Cl_2–hexane gave the pure mesylate [(2), m.p. 353–354 K]. Single crystals formed as colourless plates on diffusing liquid hexane into the solution in CH_2Cl_2.

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 $0.65 \times 0.4 \times 0.2$ [$1.0 \times 0.6 \times 0.15$] mm was mounted in a glass capillary. 3604 [9169] reflections ($-h\ \pm k\ \pm l$ [sphere]) were collected on a Siemens *R*3 diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{\max}$ 50°). Three check reflections showed no significant intensity change. No absorption correction was applied. Merging equivalents gave 3513 [2397] unique reflections ($R_{\rm int}$ 0.011 [0.024], index ranges after merging h −8 to 0 [0 to 20], k − 11 to 11 [0 to 9], l − 17 to 17 [− 12 to 12]), of which 1641 [2179] with $F > 4\sigma(F)$ were used for all calculations (program system Siemens *SHELXTL-Plus*; Sheldrick, 1990). The orientation matrix was refined from diffractometer angles of 40 [50] reflections in the 2θ range 20–24 [25]°. The structures were solved by routine direct methods and subjected to anisotropic full-matrix least-squares refinement on *F*.

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

	x	y	z	U_{eq}*
O(1)	3474 (2)	6071 (1)	4082 (1)	57 (1)
O(2)	1972 (2)	6548 (2)	5380 (1)	77 (1)
C(1)	3381 (3)	6674 (2)	5011 (1)	55 (1)
C(11)	1755 (2)	5218 (2)	3502 (1)	53 (1)
C(12)	708 (3)	6163 (2)	3158 (2)	62 (1)
F†	1873 (3)	6981 (2)	2623 (2)	84 (1)
C(13)	−1014 (3)	5239 (2)	2510 (1)	64 (1)
C(14)	−608 (3)	4174 (2)	1646 (1)	53 (1)
C(15)	524 (3)	3273 (2)	2014 (1)	61 (1)
C(16)	2241 (3)	4196 (2)	2667 (1)	58 (1)
F′‡	3377 (3)	5026 (3)	2174 (2)	80 (1)
C(17)	−2338 (3)	3259 (2)	941 (1)	62 (1)
C(18)	−3707 (3)	2301 (3)	1419 (2)	87 (1)
C(19)	−3295 (3)	4260 (3)	568 (2)	88 (1)
C(20)	−1769 (4)	2298 (3)	74 (2)	91 (1)
C(21)	5205 (2)	7529 (2)	5523 (1)	50 (1)
C(22)	6851 (2)	7355 (2)	5196 (1)	53 (1)
C(23)	8505 (2)	8200 (2)	5703 (1)	53 (1)
C(24)	8568 (2)	9262 (2)	6540 (1)	49 (1)
C(25)	6909 (3)	9424 (2)	6868 (1)	60 (1)
C(26)	5262 (3)	8562 (2)	6370 (1)	59 (1)
C(31)	10349 (3)	10197 (2)	7070 (1)	51 (1)
C(32)	11815 (3)	10675 (2)	6577 (2)	61 (1)
C(33)	13477 (3)	11556 (2)	7062 (2)	68 (1)
C(34)	13710 (3)	11952 (2)	8048 (2)	71 (1)
C(35)	12281 (3)	11484 (2)	8550 (2)	74 (1)
C(36)	10605 (3)	10622 (2)	8071 (1)	63 (1)

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

† Site occupation factor 0.537 (3).

‡ Site occupation factor 0.463 (3).

H atoms were included using a riding model. The F atom was disordered almost equally over two axial sites; the site occupation factor refined to 0.537 (3) [0.508 (4)] for the major site. The final R was 0.045 [0.042], with wR 0.051 [0.045]. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$, with g 0.000275 [0.0003]. 245 [155] parameters; S 1.6 [1.5]; max. Δ/σ 0.002 [0.001]; max. $\Delta\rho$ +0.12, −0.21 [+0.18, −0.24] e Å^{-3}.

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 Neither (1) or (2) is isostructural with its non-fluorinated analogue (Jones, Kirby & Parker, 1992*b*,*d*). (1) has no non-bonded contacts < 3.3 Å between non-H atoms. In (2) the shortest such distance is F···O(3) 3.24 Å (O at x, $1 + y$, z).

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

O(1)—C(1)	1.343 (2)	O(1)—C(11)	1.457 (2)
O(2)—C(1)	1.205 (2)	C(1)—C(21)	1.482 (2)
C(11)—C(12)	1.509 (3)	C(11)—C(16)	1.504 (3)
C(12)—F	1.419 (3)	C(16)—F′	1.373 (4)
C(1)—O(1)—C(11)	117.1 (1)	O(1)—C(1)—O(2)	123.8 (2)
O(1)—C(1)—C(21)	112.3 (2)	O(2)—C(1)—C(21)	124.0 (2)
O(1)—C(11)—C(12)	111.5 (1)	O(1)—C(11)—C(16)	107.0 (1)
C(12)—C(11)—C(16)	111.2 (2)	C(11)—C(12)—F	107.2 (2)
C(11)—C(12)—C(13)	110.2 (2)	F—C(12)—C(13)	109.2 (2)
C(11)—C(16)—F′	106.9 (2)	C(15)—C(16)—F′	110.2 (2)

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	5690 (1)	1376 (1)	7409 (1)	54 (1)
O(1)	6176 (1)	3137 (2)	7627 (2)	57 (1)
O(2)	5468 (1)	1133 (3)	8570 (2)	75 (1)
O(3)	6150 (1)	64 (2)	7005 (2)	78 (1)
C(1)	6678 (1)	3656 (3)	6787 (2)	48 (1)
C(2)	6638 (2)	5604 (3)	6705 (3)	58 (1)
F†	6871 (2)	6242 (4)	7976 (3)	68 (1)
C(3)	7192 (1)	6319 (3)	5954 (3)	57 (1)
C(4)	8077 (1)	5717 (3)	6530 (2)	47 (1)
C(5)	8089 (2)	3728 (3)	6578 (3)	59 (1)
C(6)	7537 (2)	3007 (3)	7337 (3)	60 (1)
F′‡	7820 (2)	3531 (4)	8573 (3)	75 (1)
C(7)	8693 (2)	6516 (4)	5876 (2)	55 (1)
C(8)	8612 (2)	8512 (4)	5822 (3)	72 (1)
C(9)	9564 (2)	6088 (4)	6680 (3)	84 (1)
C(10)	8559 (2)	5843 (4)	4506 (3)	81 (1)
C(11)	4819 (2)	1811 (3)	6153 (3)	64 (1)

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

† Site occupation factor 0.492 (4).

‡ Site occupation factor 0.508 (4).

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

S—O(1)	1.570 (2)	S—O(2)	1.422 (2)
S—O(3)	1.420 (2)	S—C(11)	1.737 (2)
O(1)—C(1)	1.470 (3)	C(1)—C(2)	1.499 (4)
C(1)—C(6)	1.503 (3)	C(2)—F	1.405 (4)
		C(6)—F′	1.346 (4)
O(1)—S—O(2)	104.1 (1)	O(1)—S—O(3)	109.9 (1)
O(2)—S—O(3)	119.1 (1)	O(1)—S—C(11)	104.5 (1)
O(2)—S—C(11)	109.3 (1)	O(3)—S—C(11)	108.8 (1)
S—O(1)—C(1)	121.2 (2)	O(1)—C(1)—C(2)	106.4 (2)
O(1)—C(1)—C(6)	110.0 (2)	C(2)—C(1)—C(6)	112.2 (2)
C(1)—C(2)—F	107.1 (2)	F—C(2)—C(3)	110.5 (2)
C(1)—C(6)—F′	109.1 (3)	C(5)—C(6)—F′	108.9 (2)

The axial F atom shows positional disorder in both compounds, in marked contrast to the three equatorial derivatives described in the previous paper (Jones, Kirby & Parker, 1992*a*), none of which is significantly disordered. This appears to be an intrinsic property of these systems with axial F, since all four compounds described in the following paper (Jones, Kirby & Parker, 1992*e*), derived from the epimeric alcohol (both OH and F axial) also show disorder. The apparent lengths of the chemically equivalent C—F and C—F′ bonds are also substantially different, so any interpretation of the data must be regarded with extra caution (see the discussion in the following paper). In fact we see no evidence that

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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 54759 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0059]

this disorder has any significant effect on the calculated geometrical parameters of interest: in particular, the C—O*X* bond lengths, which are the focus of interest for this investigation, fall into the expected regular pattern set by systems with no disorder when plotted as a function of the pK_a of the leaving group.

As expected, the C—F bond is fixed *gauche* to C—O by the chair conformation of the ring, as it is in the diequatorial compounds described in the previous paper (Jones, Kirby & Parker, 1992*a*), though the dihedral angle O—C—C—F is now slightly below 60° [58.0 (2) and 54.0 (3)° for (1) and (2), respectively, for the F in the major occupancy site], as the chair flattens slightly to relieve 1,3-diaxial interactions. The geometries and conformations of the esterifying groups are normal in each case. So we discuss here only the point of primary interest for this investigation, the length of the C—O*X* bond, specifically in terms of the comparison with the closely related diequatorial compounds described in the previous paper.

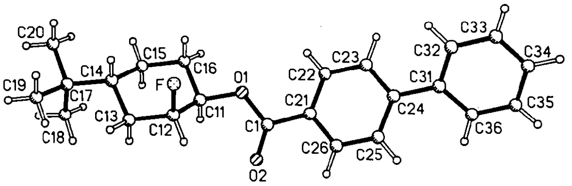

Fig. 1. Molecular structure of (1), showing the atom-numbering scheme.

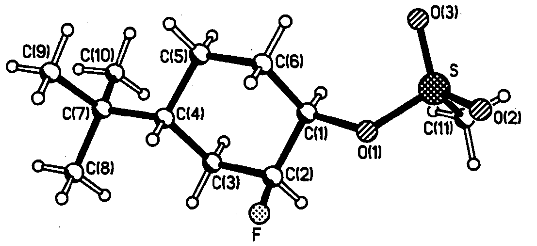

Fig. 2. Molecular structure of (2), showing the atom-numbering scheme.

The C—O ester bond length in (1) is 1.457 (2) Å, compared with a value of 1.458 (2) Å for the same ester lacking the 2-fluorine atom, and 1.453 (2) Å for the derivative with equatorial 2-fluorine. Evidently F has no significant effect on C—O bond length in this case. For the methanesulfonate ester (2), on the other hand, there does appear to be a significant effect. The C—OS bond length of 1.470 (3) Å is shorter than that for the parent mesylate [1.485 (9) Å (Jones, Kirby & Parker, 1992*d*)], or compared with our preferred value for simple cyclohexyl sulfonate esters [1.483 (4) Å (Jones, Kirby & Parker, 1992*d*)]. It is also identical, within two standard deviations, with the length of the corresponding bond in the *trans*-2-fluoronaphthalensulfonate described in the previous paper [1.466 (3) Å (Jones, Kirby & Parker, 1992*a*)].

Thus our provisional conclusion is strengthened, that the introduction of a *gauche* β-fluorine atom does cause significant shortening of the equatorial cyclohexyl C—O*X* bond in sulfonate esters, compounds with a very good leaving group. In the following papers we look for more evidence for this effect, in systems with fluorine antiperiplanar to the C—O*X* bond.

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