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Bond Length and Reactivity. The Effect of β-Fluorine. Structures of the 9-(9-Phenylxanthenyl) Ether, and the 4-Phenylbenzoate, Diphenyl Phosphate and Methanesulfonate Esters of *cis,trans*-4-*tert*-Butyl-2-fluorocyclohexanol

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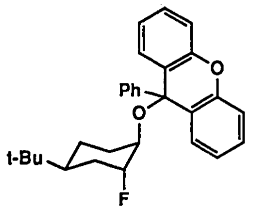
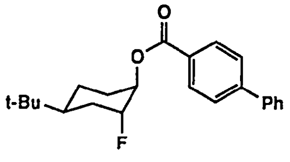
Abstract. (1*RS*,2*RS*,4*SR*)-4-*tert*-Butyl-2-fluorocyclohexyl 9-(9-phenylxanthenyl) ether, (1), $C_{29}H_{31}FO_2$, $M_r = 430.54$, triclinic, $P\bar{1}$, $a = 9.368\,(4)$, $b = 9.462\,(4)$, $c = 15.546\,(7)$ Å, $\alpha = 85.17\,(4)$, $\beta = 81.80\,(2)$, $\gamma = 61.62\,(3)°$, $V = 1200$ Å^3, $Z = 2$, $D_x = 1.192$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.07$ mm^{-1}, $F(000) = 460$, $T = 293$ K. Final $R = 0.048$ for 3160 unique observed reflections. (1*RS*,2*RS*,4*SR*)-4-*tert*-Butyl-2-fluorocyclohexyl diphenyl phosphate, (3), $C_{22}H_{28}FO_4P$, $M_r = 406.43$, clinic, $P2_1/c$, $a = 21.194\,(4)$, $b = 11.155\,(2)$, $c = 8.3306\,(15)$ Å, $\beta = 95.512\,(15)°$, $V = 1960.4$ Å^3, $Z = 4$, $D_x = 1.201$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.07$ mm^{-1}, $F(000) = 760$, $T = 293$ K. Final $R = 0.054$ for 1838 unique observed reflections. (1*RS*,2*RS*,4*SR*)-4-*tert*-Butyl-2-fluorocyclohexyl diphenyl phosphate, (3), $C_{22}H_{28}FO_4P$, $M_r = 406.43$, orthorhombic, $P2_12_12_1$, $a = 5.8904\,(15)$, $b = 10.960\,(3)$, $c = 33.090\,(8)$ Å, $V = 2136$ Å^3, $Z = 4$, $D_x = 1.264$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.16$ mm^{-1}, $F(000) = 864$, $T = 293$ K. Final $R = 0.048$ for 2106 unique observed reflections. (1*RS*,2*RS*,4*SR*)-4-*tert*-Butyl-2-fluorocyclohexyl methanesulfonate, (4), $C_{11}H_{21}FO_3S$, $M_r = 252.34$, monoclinic, $P2_1/c$, $a = 21.127\,(3)$, $b = 6.2048\,(8)$, $c = 10.4113\,(15)$ Å, $\beta = 101.427\,(11)°$, $V = 1337.7$ Å^3, $Z = 4$, $D_x = 1.253$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.23$ mm^{-1}, $F(000) = 544$, $T = 293$ K. Final $R = 0.049$ for 2558 unique observed reflections. The four structures have the ether or ester substituent and the C—F bond both axial, and thus antiperiplanar to each other. Axial fluorine shows its characteristic positional disorder in each case. The C—OX bond lengths differ scarcely at all from those in the corresponding derivatives of equatorial alcohols [Jones, Kirby & Parker (1992). *Acta Cryst.* C**48**, 852–855].

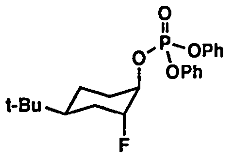
Introduction. We are interested in the effect on the length of the R—OX bond of the introduction of a strongly electron-withdrawing substituent on the β-carbon atom of the alkyl group R. We have established standard C—OX bond lengths in simple cyclohexanol derivatives (Jones, Kirby & Parker, 1992*b*,*c*,*d*), and in the previous two papers in this series we reported the structures of five esters – the 4-phenylbenzoate, the diphenyl phosphate and the 2-naphthalenesulfonate of *trans*-2-fluorocyclohexanol (Jones, Kirby & Parker, 1992*e*), and the 4-phenylbenzoate and the mesylate of *trans,cis*-4-*tert*-butyl-2-fluorocyclohexanol (Jones, Kirby & Parker, 1992*a*). The introduction of the 2-fluorine substituent has little or no effect on the length of the C—OX bond in the carboxylic or phosphate esters, but a significant shortening is observed for the sulfonate. A point of considerable interest is whether the effect of the β-fluorine substituent depends on geometry. In the compounds discussed in the two previous papers the relationship was *gauche* in each case. We report here structures for an alkyl ('pixylate') ether (1) and three esters – the 4-phenylbenzoate (2), the diphenyl phosphate (3) and the methanesulfonate (4) of *cis,trans*-4-*tert*-butyl-2-fluorocyclohexanol; all have



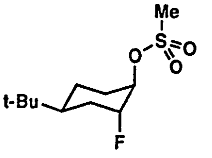
(1)



(2)



(3)



(4)

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the F atom and the C—O bond both axial, and thus antiperiplanar to each other.

Experimental. Derivatives of *cis,trans*-4-*tert*-butyl-2-fluorocyclohexanol were prepared from the mixture with *trans,trans*-5-*tert*-butyl-2-fluorocyclohexanol, described in the previous paper (Jones, Kirby & Parker, 1992*a*).

cis,trans-4-*tert*-Butyl-2-fluorocyclohexyl 9-(9-phenylxanthenyl) ether (1) was prepared by the general method of Chattophadhyaya & Reese (1978) for these conveniently crystalline 'pixylate' derivatives. Pixyl chloride [Gomberg & Cone (1909); 0.5 g, 1.7 mmol] and the mixture of alcohol isomers (0.15 g, 1.3 mmol) were added to pyridine (2 ml), and stirred for 2 h. The product was extracted three times with CH_2Cl_2, the organic layer washed in turn with 3*N* HCl, $NaHCO_3$ and brine, then dried over $MgSO_4$ before being evaporated to dryness. Purification by flash column chromatography (eluant 9:1 hexane–ethyl acetate) gave a 6:5 mixture of ethers, with the title compound in slight excess. These were separated by HPLC (eluant 9:1 hexane:CH_2Cl_2), to give the title ether (R_T 29.3 min), isolated as prisms, m.p. 434–437 K. Single crystals were grown as colourless rhombs by the liquid diffusion of petroleum ether (b.p. 313–333 K) into a solution in diethyl ether.

cis,trans-4-*tert*-Butyl-2-fluorocyclohexyl 4-phenylbenzoate (2) was prepared by the method described previously for the parent ester (F absent: Jones, Kirby & Parker, 1992*b*). The mixture of products was purified by flash column chromatography (eluant CH_2Cl_2) and recrystallization from methanol, which gave a 6:5 mixture of esters, with the desired isomer present in slight excess. Separation by HPLC (eluant 3:1 CH_2Cl_2–hexane) gave the title compound [(2), R_T 47 min] as prisms, m.p. 387–388 K. Single crystals, in the form of thin colourless plates, were grown by diffusion of liquid hexane into a solution in CH_2Cl_2.

cis,trans-4-*tert*-Butyl-2-fluorocyclohexyl diphenyl phosphate (3) was prepared by the general method described previously for phosphate esters (Jones, Kirby & Parker, 1992*g*). Flash column chromatography (eluant 3:1 hexane–ethyl acetate) gave a mixture of phosphate esters (88%). These were separated by HPLC (eluant 11% ethyl acetate in hexane) to give the title compound [(3), R_T 25.4 min], m.p. 346–347 K. Single crystals were obtained as colourless needles, by the diffusion of liquid petroleum ether (b.p. 313–333 K) into solution in diethyl ether.

cis,trans-4-*tert*-Butyl-2-fluorocyclohexyl methanesulfonate (4). The mixture of mesylates (68%), was prepared by the general method already described (Kirby, Parker & Raithby, 1992), followed by recrystallization from CH_2Cl_2–hexane. Two further recrystallizations from CH_2Cl_2–hexane gave the single mesylate (4) as prisms, m.p. 370–372 K. Single crystals were grown as colourless blocks by the diffusion of liquid hexane into the solution in CH_2Cl_2.

(1). A crystal 1.0 × 0.6 × 0.5 mm was mounted in a glass capillary. 8447 reflections (a complete 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 or extinction correction was applied. Merging equivalents gave 4245 unique reflections ($R_{\rm int}$ 0.028, index ranges after merging h 0 to 11, k −11 to 11, l −18 to 18), of which 3160 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens *SHELXTL-Plus*; Sheldrick, 1990). Cell constants were refined from diffractometer angles of 46 reflections in the 2θ range 20–23°. The structure of (1) 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 F atom was disordered over two axial sites, with site occupation factor (s.o.f.) 0.611 (4) for the major component. The final *R* was 0.048, with *wR* 0.062. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$, with g 0.00025. 299 parameters; *S* 2.4; max. Δ/σ 0.002; max. $\Delta\rho$ +0.16, −0.18 e Å^{-3}.

(2). As for (1), with following differences. Crystal 0.75 × 0.45 × 0.08 mm, 5054 reflections. $R_{\rm int}$ 0.027, $-h$ $+k$ $+l$ and some $+h$ equivalents, 3439 unique, 1838 > $3\sigma(F)$, index ranges h 0 to 25, k 0 to 13, l −9 to 9. The crystal diffracted weakly. Cell constants refined from $\pm\omega$ angles of 30 reflections in the 2θ range 20–23° on a Stoe–Siemens diffractometer (same crystal). Axial F disorder with s.o.f. of major site 0.768 (5). Final *R* 0.054, *wR* 0.052, *g* 0.0002. 240 parameters; *S* 1.7; max. Δ/σ 0.001, max. $\Delta\rho$ +0.18, −0.18 e Å^{-3}.

(3). As for (1), with following differences. Crystal 0.8 × 0.1 × 0.15 mm, 3900 reflections ($\pm h$ $+k$ $+l$), 3661 unique ($R_{\rm int}$ 0.023), 2106 > $3\sigma(F)$, index ranges h −7 to 7, k 0 to 13, l 0 to 39. The crystal diffracted weakly. Cell constants from 50 reflections in the 2θ range 20–23°. Axial *F* disorder with s.o.f. of major site 0.654 (6). Absolute structure not determined [η −0.2 (5)]. Final *R* 0.048, *wR* 0.046 for 258 parameters, *g* 0.00035. 240 parameters; *s* 1.2; max. Δ/σ 0.001; max. $\Delta\rho$ +0.29, −0.31 e Å^{-3}.

(4). As for (1), with following differences. Crystal 1.0 × 0.6 × 0.4 mm, Stoe–Siemens diffractometer, $2\theta_{\max}$ 55°, 4396 reflections ($R_{\rm int}$ 0.014, $\pm h$ $+k$ $+l$ and some $+h$ $-k$ $-l$ equivalents), 3050 unique, 2558 > $4\sigma(F)$, index ranges h 0 to 27, k 0 to 8, l −13 to 13. Cell constants from $\pm\omega$ angles of 54 reflections in the 2θ range 20–23°. Axial *F* disorder with s.o.f. of major site 0.746 (3). Final *R* 0.049, *wR* 0.066 for 150 parameters, *g* 0.00025. *S* 2.7; max. Δ/σ 0.001; max. $\Delta\rho$ +0.34, −0.32 e Å^{-3}.

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

	x	y	z	U_{eq}*
C(1)	4928 (2)	1760 (2)	6784 (1)	47 (1)
O(1)	5606 (1)	1940 (1)	7526 (1)	57 (1)
O(2)	6786 (2)	−991 (1)	5626 (1)	63 (1)
C(11)	7107 (3)	631 (2)	7750 (2)	72 (1)
C(12)	6894 (3)	473 (3)	8720 (2)	87 (1)
C(13)	6838 (3)	1882 (3)	9167 (1)	72 (1)
C(14)	8328 (2)	2118 (2)	8870 (1)	59 (1)
C(15)	8476 (3)	2309 (3)	7885 (1)	67 (1)
C(16)	8546 (3)	932 (3)	7435 (2)	82 (1)
C(17)	8398 (3)	3451 (3)	9343 (1)	65 (1)
C(18)	8091 (3)	3273 (3)	10327 (2)	97 (2)
C(19)	10131 (3)	3261 (3)	9140 (2)	92 (2)
C(20)	7189 (3)	5123 (3)	9064 (2)	103 (2)
F†	8250 (4)	−990 (3)	8928 (2)	137 (2)
F′‡	9903 (4)	−455 (5)	7624 (3)	115 (3)
C(21)	4807 (2)	208 (2)	6874 (1)	48 (1)
C(22)	5716 (2)	−1045 (2)	6310 (1)	49 (1)
C(23)	5636 (3)	−2478 (2)	6415 (2)	66 (1)
C(24)	4625 (3)	−2651 (3)	7085 (2)	76 (1)
C(25)	3693 (3)	−1429 (3)	7658 (2)	80 (1)
C(26)	3781 (3)	−5 (2)	7547 (1)	68 (1)
C(31)	5995 (2)	1759 (2)	5956 (1)	48 (1)
C(32)	6882 (2)	419 (2)	5450 (1)	49 (1)
C(33)	7952 (2)	389 (3)	4729 (1)	65 (1)
C(34)	8131 (3)	1732 (3)	4500 (2)	71 (1)
C(35)	7239 (3)	3104 (3)	4980 (2)	75 (1)
C(36)	6188 (3)	3112 (2)	5694 (2)	68 (1)
C(41)	3233 (2)	3209 (2)	6806 (1)	46 (1)
C(42)	2673 (2)	4441 (2)	7389 (1)	54 (1)
C(43)	1121 (3)	5722 (2)	7381 (2)	67 (1)
C(44)	109 (3)	5794 (2)	6813 (2)	69 (1)
C(45)	645 (2)	4574 (3)	6226 (2)	68 (1)
C(46)	2205 (2)	3301 (2)	6219 (1)	58 (1)

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

† Site occupation factor 0.611 (4).

‡ Site occupation factor 0.359 (4).

Discussion. Final atomic coordinates for (1), (2), (3) and (4) are given in Tables 1–4, and derived parameters in Table 5.* Plots of (1)–(4), showing the atom-numbering schemes, appear as Figs. 1–4. The structures of the non-fluorinated analogues of (2) and (4) were reported in earlier papers in this series (Jones, Kirby & Parker, 1992*b*,*d*). The ester (2) crystallizes in the same space group as the parent compound, but is not isostructural whereas the two mesylates are isostructural. In (2) the molecules are arranged approximately parallel to the z axis, with the biphenyl groups (inter-ring torsion angle 26°) occupying the region near $z = 0.5$: in (4) the methanesulfonate groups occupy the region near $x = 0.5$. Short non-bonded contacts are observed only in (4): F···O(1) 3.28, C(2)···O(3) 3.30 (second atoms at

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

	x	y	z	U_{eq}*
O(1)	7228 (1)	4494 (2)	5229 (3)	62 (1)
O(2)	6962 (1)	2923 (2)	6725 (3)	87 (1)
C(1)	6819 (2)	3652 (3)	5682 (4)	63 (1)
C(11)	7837 (1)	4576 (3)	6196 (4)	64 (1)
C(12)	8280 (2)	3630 (3)	5679 (4)	71 (1)
F†	8801 (1)	3642 (2)	6878 (3)	95 (1)
C(13)	8510 (1)	3844 (3)	4061 (4)	61 (1)
C(14)	8805 (1)	5086 (2)	3926 (3)	51 (1)
C(15)	8308 (1)	6007 (3)	4298 (4)	61 (1)
C(16)	8082 (2)	5825 (3)	5936 (4)	68 (1)
F′‡	8542 (5)	5961 (9)	7083 (12)	108 (4)
C(17)	9128 (1)	5309 (3)	2372 (4)	59 (1)
C(18)	9624 (2)	4329 (3)	2178 (5)	90 (2)
C(19)	8662 (2)	5337 (4)	887 (4)	98 (2)
C(20)	9489 (2)	6507 (3)	2502 (5)	89 (2)
C(21)	6184 (1)	3755 (3)	4783 (4)	53 (1)
C(22)	6044 (2)	4538 (3)	3504 (4)	59 (1)
C(23)	5447 (2)	4604 (3)	2728 (4)	59 (1)
C(24)	4954 (1)	3889 (2)	3195 (3)	52 (1)
C(25)	5099 (2)	3125 (3)	4493 (4)	64 (1)
C(26)	5703 (2)	3051 (3)	5258 (4)	64 (1)
C(31)	4310 (1)	3922 (3)	2326 (4)	56 (1)
C(32)	4087 (2)	4923 (3)	1469 (4)	70 (1)
C(33)	3493 (2)	4939 (4)	620 (5)	86 (2)
C(34)	3112 (2)	3944 (5)	627 (5)	95 (2)
C(35)	3323 (2)	2954 (4)	1472 (6)	102 (2)
C(36)	3912 (2)	2940 (3)	2308 (5)	77 (1)

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

† Site occupation factor 0.768 (5).

‡ Site occupation factor 0.232 (5).

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

	x	y	z	U_{eq}*
P	5094 (2)	6261 (1)	1181.3 (3)	47 (1)
O(1)	4297 (4)	6030 (3)	1622 (1)	51 (1)
O(2)	3342 (5)	5609 (3)	893 (1)	48 (1)
O(3)	4403 (5)	7636 (3)	1113 (1)	50 (1)
O(4)	7455 (5)	5949 (3)	1114 (1)	60 (1)
C(11)	1964 (7)	6220 (4)	1762 (1)	47 (2)
C(12)	1853 (9)	7436 (4)	1982 (1)	60 (2)
F†	−426 (8)	7626 (5)	2058 (1)	88 (2)
C(13)	3180 (8)	7449 (4)	2369 (1)	51 (2)
C(14)	2559 (7)	6407 (4)	2655 (1)	42 (1)
C(15)	2803 (9)	5198 (4)	2426 (1)	52 (2)
C(16)	1427 (9)	5173 (5)	2037 (1)	59 (2)
F′‡	−840 (15)	5253 (8)	2139 (3)	72 (3)
C(17)	3794 (7)	6446 (5)	3068 (1)	51 (2)
C(18)	2996 (9)	5419 (5)	3336 (1)	75 (2)
C(19)	6388 (7)	6347 (6)	3017 (2)	74 (2)
C(20)	3270 (9)	7646 (5)	3282 (1)	71 (2)
C(21)	3314 (8)	4346 (4)	817 (1)	42 (2)
C(22)	5018 (9)	3801 (5)	598 (1)	56 (2)
C(23)	4821 (10)	2572 (5)	506 (1)	68 (2)
C(24)	2953 (10)	1918 (5)	630 (2)	71 (2)
C(25)	1261 (9)	2483 (5)	844 (1)	63 (2)
C(26)	1427 (8)	3703 (5)	937 (1)	51 (2)
C(31)	4624 (9)	8202 (4)	728 (1)	45 (2)
C(32)	2838 (9)	8138 (4)	465 (2)	57 (2)
C(33)	3042 (10)	8711 (5)	92 (2)	70 (2)
C(34)	4981 (13)	9335 (5)	−1 (2)	76 (2)
C(35)	6754 (11)	9399 (5)	272 (2)	76 (2)
C(36)	6579 (8)	8820 (5)	643 (2)	60 (2)

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

† Site occupation factor 0.654 (6).

‡ Site occupation factor 0.346 (6).

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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 54760 (83 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0060]

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

	x	y	z	U_{eq}*
S	4127.0 (2)	4323 (1)	6365.6 (4)	62 (1)
O(1)	3427.7 (6)	4155 (2)	5513 (1)	66 (1)
O(2)	4422.6 (8)	6258 (3)	6073 (2)	91 (1)
O(3)	4050.5 (7)	3967 (3)	7667 (1)	96 (1)
F†	2718 (1)	4376 (3)	2103 (2)	86 (1)
F′‡	2852 (3)	8216 (10)	3139 (6)	93 (2)
C(1)	3273 (1)	5145 (4)	4211 (2)	61 (1)
C(2)	2799 (1)	3605 (3)	3395 (2)	60 (1)
C(3)	2162 (1)	3517 (3)	3831 (2)	53 (1)
C(4)	1850 (1)	5739 (3)	3895 (2)	48 (1)
C(5)	2335 (1)	7199 (3)	4770 (2)	67 (1)
C(6)	2974 (1)	7326 (4)	4326 (2)	77 (1)
C(7)	1178 (1)	5641 (3)	4270 (2)	57 (1)
C(8)	704 (1)	4400 (4)	3224 (3)	81 (1)
C(9)	911 (1)	7939 (4)	4331 (3)	87 (1)
C(10)	1211 (1)	4541 (4)	5602 (2)	79 (1)
C(11)	4530 (1)	2160 (4)	5834 (2)	80 (1)

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

† Site occupation factor 0.746 (3).

‡ Site occupation factor 0.254 (3).

x, $0.5 - y$, $-0.5 + z$), C(5)···F 3.21 Å (x, $1.5 - y$, $0.5 + z$).

The axial F atom shows positional disorder in all four compounds, just as it did in the two structures also with axial F, described in the previous paper (Jones, Kirby & Parker, 1992*a*). As with those structures, we see no evidence for a significant effect of the disorder on the geometrical parameters of interest for this investigation. Any such effect should be readily detected in the context of a close examination of a series of related structures with and without disorder [see the plot in the following paper (Jones, Kirby & Parker, 1992*f*)]. So we are reasonably confident that our calculated C—OX bond lengths in particular can be taken at face value. The C—F bond lengths, on the other hand, may be influenced by the superimposed C—H of the alternative disorder component (the larger the s.o.f. of the major site the less likely this is), and do show signs of possible scatter. Those for F in the major occupancy site lie, with one exception, within two standard deviations of the value of 1.413 (4) Å measured for axial C—F in the absence of disorder in the following paper (Jones, Kirby & Parker, 1992*f*). The exception is the least accurate value in this paper, 1.382 (7) Å for (3). The mean value for the length of the alkyl C—F for compounds in the Cambridge Structural Database (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) is 1.399 ± 0.017 Å, though this makes no distinction between primary and secondary alkyl fluorides. All our observed values for F in the major occupancy site fall within this range; so we have only minor reservations about using bond-length values, and less about bond and dihedral angles referring even to this site.

Table 5. *Selected bond lengths* (Å) *and angles* (°) *for* (1), (2), (3) *and* (4)

Compound (1)			
C(1)—O(1)	1.451 (3)	C(1)—C(21)	1.519 (3)
C(1)—C(31)	1.513 (2)	C(1)—C(41)	1.525 (2)
O(1)—C(11)	1.430 (2)	O(2)—C(22)	1.369 (2)
O(2)—C(32)	1.382 (3)	C(11)—C(12)	1.497 (4)
C(11)—C(16)	1.515 (4)		
C(12)—F	1.416 (3)	C(16)—F′	1.372 (4)
O(1)—C(1)—C(21)	110.1 (1)	O(1)—C(1)—C(31)	109.7 (2)
C(21)—C(1)—C(31)	110.1 (1)	O(1)—C(1)—C(41)	105.1 (1)
C(21)—C(1)—C(41)	110.6 (2)	C(31)—C(1)—C(41)	111.1 (1)
C(1)—O(1)—C(11)	117.9 (1)	C(22)—O(2)—C(32)	118.9 (1)
O(1)—C(11)—C(12)	105.7 (2)	O(1)—C(11)—C(16)	111.6 (2)
C(12)—C(11)—C(16)	111.4 (2)	C(11)—C(12)—C(13)	112.3 (2)
C(11)—C(12)—F	105.5 (2)	C(13)—C(12)—F	110.8 (3)
C(11)—C(16)—F′	105.5 (3)	C(15)—C(16)—F′	109.3 (3)
Compound (2)			
O(1)—C(1)	1.356 (4)	O(1)—C(11)	1.457 (3)
O(2)—C(1)	1.207 (4)	C(1)—C(21)	1.481 (4)
C(11)—C(12)	1.503 (5)	C(11)—C(16)	1.510 (4)
C(12)—F	1.417 (4)	C(16)—F′	1.306 (10)
C(1)—O(1)—C(11)	116.4 (2)	O(1)—C(1)—O(2)	123.0 (3)
O(1)—C(1)—C(21)	112.3 (3)	O(2)—C(1)—C(21)	124.7 (3)
O(1)—C(11)—C(12)	109.9 (2)	O(1)—C(11)—C(16)	106.1 (2)
C(12)—C(11)—C(16)	111.9 (3)	C(11)—C(12)—F	104.9 (3)
C(11)—C(12)—C(13)	114.4 (3)	F—C(12)—C(13)	109.5 (3)
Compound (3)			
P—O(1)	1.554 (3)	P—O(2)	1.576 (3)
P—O(3)	1.577 (3)	P—O(4)	1.450 (3)
O(1)—C(11)	1.465 (5)	O(2)—C(21)	1.407 (5)
O(3)—C(31)	1.422 (5)	C(11)—C(12)	1.520 (7)
C(11)—C(16)	1.498 (7)	C(12)—F	1.382 (7)
		C(16)—F′	1.381 (10)
O(1)—P—O(2)	107.3 (2)	O(1)—P—O(3)	102.3 (2)
O(2)—P—O(3)	100.2 (2)	O(1)—P—O(4)	113.3 (2)
O(2)—P—O(4)	115.3 (2)	O(3)—P—O(4)	116.8 (2)
P—O(1)—C(11)	123.8 (2)	P—O(2)—C(21)	124.2 (3)
P—O(3)—C(31)	121.4 (3)	O(1)—C(11)—C(12)	108.4 (4)
O(1)—C(11)—C(16)	106.3 (4)	C(12)—C(11)—C(16)	111.8 (4)
C(11)—C(12)—F	105.1 (4)	C(11)—C(12)—C(13)	113.3 (4)
F—C(12)—C(13)	110.5 (4)	C(12)—C(13)—C(14)	113.4 (4)
C(11)—C(16)—F′	107.7 (5)	C(15)—C(16)—F′	107.8 (5)
Compound (4)			
S—O(1)	1.569 (1)	S—O(2)	1.414 (2)
S—O(3)	1.413 (2)	S—C(11)	1.737 (3)
O(1)—C(1)	1.465 (2)	F—C(2)	1.406 (2)
F′—C(6)	1.331 (6)	C(1)—C(2)	1.517 (3)
O(1)—S—O(2)	109.9 (1)	O(1)—S—O(3)	104.9 (1)
O(2)—S—O(3)	118.6 (1)	O(1)—S—C(11)	103.5 (1)
O(2)—S—C(11)	108.8 (1)	O(3)—S—C(11)	109.9 (1)
S—O(1)—C(1)	120.5 (1)	O(1)—C(1)—C(2)	104.8 (2)
O(1)—C(1)—C(6)	108.9 (2)	C(2)—C(1)—C(6)	111.7 (2)
F—C(2)—C(1)	105.3 (2)	F—C(2)—C(3)	110.7 (2)
F′—C(6)—C(1)	107.9 (3)	F′—C(6)—C(5)	106.5 (3)

As expected, the C—F bond is fixed antiperiplanar to C—O by the chair conformation of the ring, though the dihedral angles O—C—C—F are actually significantly below 180° [169.7 (3), 169.3 (2), 172.5 (3) and 171.9 (2)° for (1)–(4), respectively], as the chair conformation flattens slightly to relieve 1,3-diaxial interactions. The geometries and conformations of the esterifying groups are normal in each

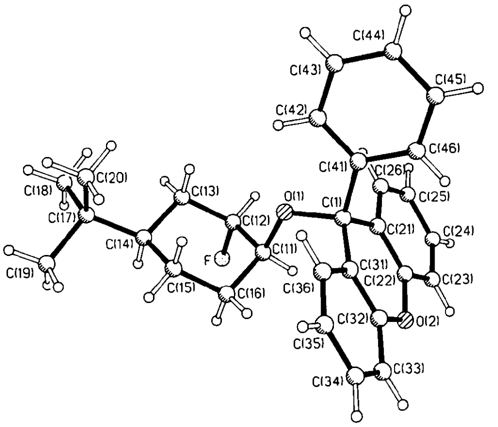

Fig. 1. Molecular structure of (1), showing the atom-numbering scheme.

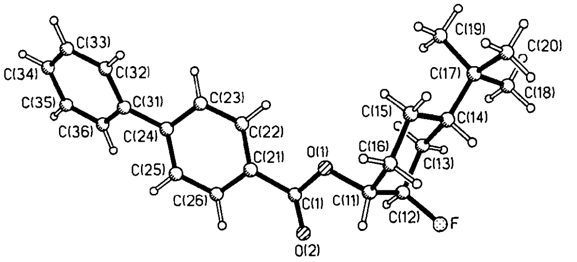

Fig. 2. Molecular structure of (2), showing the atom-numbering scheme.

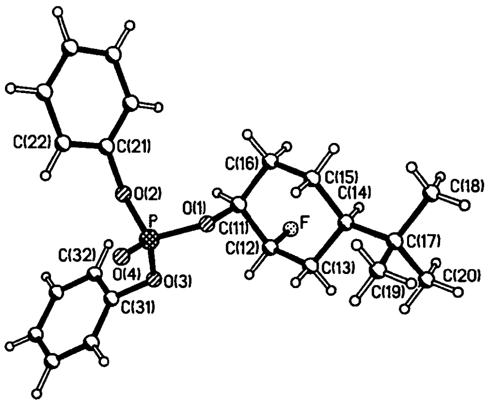

Fig. 3. Molecular structure of (3), showing the atom-numbering scheme.

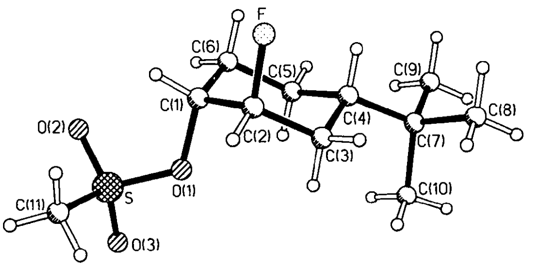

Fig. 4. Molecular structure of (4), showing the atom-numbering scheme.

case, and generally similar to those for the same groups in equatorial positions observed in earlier papers of this series. So we can concentrate on the point of primary interest for this investigation, the length of the C—O*X* bond, particularly in terms of the comparison with the equatorial compounds described in previous papers.

The results in this and previous papers show clearly that the effect of a β-fluorine is independent of geometry. Thus C—O bond lengths for the diaxial derivatives measured in this paper are identical, within experimental error, with those measured previously for the corresponding diequatorial, or axial–equatorial isomers. We have made the comparison already for equatorial C—O*X* with F axial or equatorial (Jones, Kirby & Parker, 1992*a*), so here compare specifically *trans* diequatorial (Jones, Kirby & Parker, 1992*e*) and *trans* diaxial derivatives (this paper), where the dihedral angle between the C—O*X* and C—F bonds changes from near 60° to near 180°.

The C—O ester bond length in (2) is 1.457 (5) Å, compared with 1.453 (2) Å in the corresponding diequatorial ester. Similarly, the C—OP bond length in (3) is 1.465 (5) Å, compared with 1.463 (3) Å in the corresponding diequatorial ester. And the C—OS bond length in (4) is also 1.465 (5) Å, compared with 1.466 (3) Å in the corresponding diequatorial (2-naphthalenesulfonate) ester. In all three systems, the introduction of the β-fluorine atom is associated with a significant shortening of the sulfonate C—O bond, but not of the C—O ester bond.

The C—O*X* bond length in (1)–(4) depends, as expected (Jones & Kirby, 1979, 1984) on the electron-withdrawing capability of the group *X*. This question is taken up in more detail in the following paper, in the light of all the data available.

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

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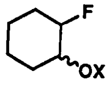
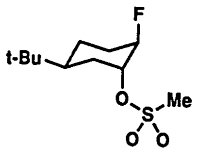
Abstract. (1*RS*,2*RS*,5*SR*)-5-*tert*-Butyl-2-fluorocyclohexyl methanesulfonate, $C_{11}H_{21}FO_3S$, $M_r = 252.35$, orthorhombic, *Pbca*, $a = 10.249\,(2)$, $b = 8.853\,(2)$, $c = 29.687\,(4)$ Å, $V = 2693$ Å^3, $Z = 8$, $D_x = 1.245$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.23$ 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.* C**48**, 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.

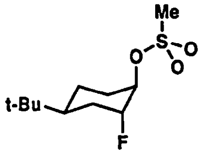
Introduction. In the previous papers in this series we have reported the structures of a total of nine derivatives (1) of cyclohexanol with fluorine in the 2-position in a geometrically defined, *gauche* or antiperiplanar relationship to the C—O*X* bond. The introduction of the 2-fluorine substituent 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

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