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Bond Length and Reactivity. The Effect of β-Fluorine. Structures of the 4-Phenylbenzoate, the Diphenyl Phosphate and the 2-Naphthalenesulfonate Esters of *trans*-2-Fluorocyclohexanol

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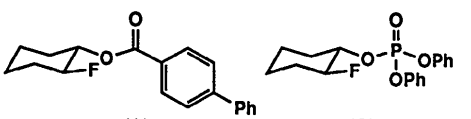
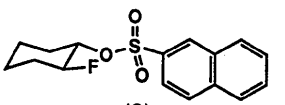
Abstract. *trans*-2-Fluorocyclohexyl 4-phenylbenzoate, (1), $C_{19}H_{19}FO_2$, $M_r = 298.36$, monoclinic, $P2_1/n$, $a = 6.9710$ (1), $b = 9.3896$ (11), $c = 23.826$ (4) Å, $\beta = 93.518$ (12)°, $V = 1556.6$ Å^3, $Z = 4$, $D_x = 1.273$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.08$ mm^{-1}, $F(000) = 632$, $T = 293$ K. Final $R = 0.062$ for 2396 unique observed reflections. *trans*-2-Fluorocyclohexyl diphenyl phosphate, (2), $C_{18}H_{20}FO_4P$, $M_r = 350.32$, monoclinic, Cc, $a = 16.644$ (5), $b = 9.277$ (3), $c = 12.048$ (4) Å, $\beta = 109.80$ (3)°, $V = 1750$ Å^3, $Z = 4$, $D_x = 1.329$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.18$ mm^{-1}, $F(000) = 736$, $T = 293$ K. Final $R = 0.029$ for 2977 unique observed reflections. *trans*-2-Fluorocyclohexyl 2-naphthalenesulfonate, (3), $C_{16}H_{17}FO_3S$, $M_r = 308.37$, monoclinic, $P2_1/c$, $a = 11.7709$ (15), $b = 15.601$ (2), $c = 8.2119$ (12) Å, $\beta = 94.728$ (15)°, $V = 1502.9$ Å^3, $Z = 4$, $D_x = 1.363$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.22$ mm^{-1}, $F(000) = 648$, $T = 293$ K. Final $R = 0.053$ for 2098 unique observed reflections. The three related structures have both substituents equatorial, and C—F thus *gauche* to the C—O*X* bond. The introduction of the 2-fluorine atom is associated with a significant shortening of the C—O bond only 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*. In previous papers (Jones, Dölle, Kirby & Parker, 1992*a*,*b*) we could identify no clear-cut effect of a β-fluorine atom on the length of the C—O*X* bond in a series of acyclic compounds, and here begin an examination of systems of fixed conformation. We have established standard C—O*X* bond lengths in simple cyclohexanol derivatives (Jones, Kirby & Parker, 1992*a*). In this paper we report the structures of three esters [(1)–(3)] of *trans*-2-fluorocyclohexanol, derived from acids of a wide range of pK_a.



(1) (2)



(3)

Experimental. *trans*-2-Fluorocyclohexanol was prepared from cyclohexene oxide and HF–pyridine by the method of Olah & Meidar (1978). The yellow oil produced was distilled to give a colourless oil (70%), b.p. 341–345 K/4 mm Hg (lit. m.p. 292–294 K; Farges & Kergomard, 1963).

trans-2-Fluorocyclohexyl 4-phenylbenzoate (1) was prepared from the alcohol by the method described previously for the 4-*tert*-butyl esters (Jones, Kirby & Parker, 1992*b*). Purification by flash column chromatography (eluant CH_2Cl_2) and recrystallization from CH_2Cl_2–light petroleum (b.p. 313–333 K) gave platelets (m.p. 425–427 K, 77%) Single crystals, in the form of colourless tablets, were grown by vapour diffusion of petroleum ether into a solution in CH_2Cl_2.

trans-2-Fluorocyclohexyl diphenyl phosphate (2). The general method for the preparation of phosphate esters has been described in Jones, Kirby & Parker (1992*c*). Purification by flash column chromatography (eluant CH_2Cl_2), and recrystallization from diethyl ether–pentane at 277 K gave prisms (m.p. 329–330.5 K, 66%). Single crystals (colourless rhombs) were grown by the diffusion of liquid pentane into a solution in diethyl ether.

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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)	5100 (3)	6036 (2)	897 (1)	50 (1)
C(2)	5190 (3)	7534 (2)	694 (1)	60 (1)
C(3)	6436 (4)	7646 (3)	197 (1)	71 (1)
C(4)	8433 (4)	7058 (3)	339 (1)	82 (1)
C(5)	8346 (3)	5556 (3)	562 (1)	75 (1)
C(6)	7084 (3)	5467 (3)	1061 (1)	68 (1)
F	3341 (2)	8001 (2)	530 (1)	95 (1)
O(1)	3905 (2)	6033 (2)	1376 (1)	57 (1)
C(10)	2918 (3)	4830 (2)	1467 (1)	51 (1)
O(10)	3066 (2)	3765 (2)	1188 (1)	72 (1)
C(11)	1641 (3)	4973 (2)	1937 (1)	45 (1)
C(12)	1572 (3)	6209 (2)	2256 (1)	52 (1)
C(13)	312 (3)	6310 (2)	2681 (1)	52 (1)
C(14)	−932 (3)	5202 (2)	2792 (1)	45 (1)
C(15)	−825 (3)	3961 (2)	2474 (1)	52 (1)
C(16)	438 (3)	3848 (2)	2053 (1)	51 (1)
C(21)	−2350 (3)	5345 (2)	3232 (1)	49 (1)
C(22)	−1901 (3)	6083 (2)	3730 (1)	58 (1)
C(23)	−3232 (4)	6206 (3)	4133 (1)	69 (1)
C(24)	−5020 (4)	5603 (3)	4049 (1)	72 (1)
C(25)	−5495 (3)	4879 (3)	3557 (1)	69 (1)
C(26)	−4176 (3)	4753 (2)	3154 (1)	58 (1)

* 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* (2)

	x	y	z	U_{eq}*
P	5000	9092.9 (4)	5000	43 (1)
O(1)	5475 (1)	10266 (2)	5900 (1)	71 (1)
O(2)	4442 (1)	8238 (2)	5609 (1)	62 (1)
O(3)	4286 (1)	10048 (1)	4115 (1)	51 (1)
O(4)	5520 (1)	8203 (1)	4522 (1)	50 (1)
C(11)	6407 (1)	10342 (2)	6407 (2)	51 (1)
C(12)	6696 (2)	11795 (3)	6146 (2)	65 (1)
F	6473 (2)	11942 (2)	4937 (1)	119 (1)
C(13)	7644 (2)	11969 (3)	6722 (2)	72 (1)
C(14)	7904 (2)	11728 (3)	8032 (2)	78 (1)
C(15)	7619 (2)	10286 (3)	8305 (2)	83 (1)
C(16)	6663 (2)	10102 (3)	7716 (2)	70 (1)
C(21)	4722 (1)	6945 (2)	6230 (2)	48 (1)
C(22)	4637 (1)	5682 (2)	5619 (2)	61 (1)
C(23)	4858 (2)	4407 (3)	6233 (3)	76 (1)
C(24)	5148 (2)	4412 (3)	7440 (3)	81 (1)
C(25)	5242 (2)	5686 (3)	8043 (2)	74 (1)
C(26)	5020 (1)	6982 (2)	7447 (2)	59 (1)
C(31)	3658 (1)	9423 (2)	3129 (2)	44 (1)
C(32)	3864 (1)	9088 (2)	2154 (2)	53 (1)
C(33)	3235 (2)	8586 (3)	1159 (2)	68 (1)
C(34)	2409 (2)	8456 (3)	1143 (2)	73 (1)
C(35)	2214 (1)	8794 (3)	2127 (3)	76 (1)
C(36)	2844 (1)	9279 (2)	3150 (2)	60 (1)

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

trans-2-Fluorocyclohexyl 2-naphthalenesulfonate (3) was prepared by our general method for sulfonate esters (Jones, Schmidt-Bäse, Edwards & Kirby, 1992). Purification by flash column chromatography (eluant CH_2Cl_2) and recrystallization from CH_2Cl_2 gave prisms (m.p. 338–340 K, 54%). Single crystals were grown by liquid diffusion of pentane into a solution in diethyl ether, and formed colourless prisms.

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

	x	y	z	U_{eq}*
S	2621.2 (6)	1098.3 (5)	6208.1 (8)	66 (1)
O(1)	3329 (1)	661 (1)	4876 (2)	66 (1)
O(2)	3277 (2)	1773 (1)	6995 (2)	75 (1)
O(3)	2267 (2)	395 (2)	7131 (3)	92 (1)
C(1)	3919 (2)	1199 (2)	3748 (3)	57 (1)
C(2)	3832 (2)	739 (2)	2132 (3)	67 (1)
F	2688 (2)	679 (2)	1562 (2)	106 (1)
C(3)	4487 (3)	1189 (2)	898 (3)	73 (1)
C(4)	5716 (2)	1311 (2)	1521 (3)	78 (1)
C(5)	5796 (2)	1785 (2)	3137 (3)	82 (1)
C(6)	5146 (2)	1311 (2)	4373 (3)	69 (1)
C(11)	1446 (2)	1544 (2)	5055 (3)	57 (1)
C(12)	1292 (2)	2406 (2)	5023 (3)	55 (1)
C(13)	333 (2)	2772 (2)	4125 (3)	56 (1)
C(14)	131 (3)	3657 (2)	4120 (3)	71 (1)
C(15)	−813 (3)	3989 (3)	3289 (4)	90 (1)
C(16)	−1571 (3)	3458 (3)	2395 (5)	99 (2)
C(17)	−1395 (3)	2599 (3)	2339 (4)	87 (1)
C(18)	−450 (2)	2225 (2)	3247 (3)	64 (1)
C(19)	−261 (3)	1324 (2)	3314 (4)	75 (1)
C(20)	657 (3)	986 (2)	4192 (3)	71 (1)

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

Crystals were mounted in glass capillaries. For (1): crystal 0.7 × 0.45 × 0.15 mm. 5538 reflections ($\pm h + k + l$ and some $\pm h - k + l$ equivalents) were collected on a Stoe–Siemens diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{max}$ 55°). Three check reflections showed no significant intensity change. No absorption or extinction correction was applied. Merging equivalents gave 3543 unique reflections (R_{int} 0.021, index ranges after merging h 0 to 9, k 0 to 12, l −30 to 30), of which 2396 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 52 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 final R was 0.062, with wR 0.058. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$. 199 parameters; S 2.1; max. Δ/σ 0.001; max. $\Delta\rho$ +0.19, −0.34 e $Å^{-3}$.

(2). As for (1), with following differences. Crystal 1.0 × 0.8 × 0.6 mm, Siemens $R3$ diffractometer, $2\theta_{max}$ 50°, 3105 reflections $\pm h + k \pm l$, 3099 unique, $2977 > 4\sigma(F)$, index ranges h −19 to 19, k 0 to 11, l −14 to 14. Cell constants refined from diffractometer angles of 48 reflections in the 2θ range 20–23°. The absolute structure was determined by an η refinement [$\eta = -1.02$ (14)], whereupon the structure was inverted for the final cycles. R 0.029, wR 0.036, 215 parameters, S 1.9; max. Δ/σ 0.004; max. $\Delta\rho$ +0.29, −0.44 e $Å^{-3}$.

(3). As for (1), with following differences. Crystal 0.75 × 0.3 × 0.15 mm, $2\theta_{max}$ 50°, 3799 reflections

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

Compound (1)			
C(1)—C(2)	1.491 (3)	C(1)—C(6)	1.512 (3)
C(1)—O(1)	1.453 (2)	C(2)—F	1.394 (3)
C(10)—O(10)	1.209 (3)	O(1)—C(10)	1.347 (3)
C(10)—C(11)	1.479 (3)		
C(2)—C(1)—C(6)	111.2 (2)	C(2)—C(1)—O(1)	107.1 (2)
C(6)—C(1)—O(1)	110.9 (2)	C(1)—C(2)—C(3)	111.0 (2)
C(1)—C(2)—F	109.4 (2)	C(3)—C(2)—F	108.9 (2)
Compound (2)			
P—O(1)	1.551 (2)	P—O(2)	1.578 (2)
P—O(3)	1.574 (1)	P—O(4)	1.449 (1)
O(1)—C(11)	1.463 (2)	O(2)—C(21)	1.408 (2)
O(3)—C(31)	1.413 (2)	C(11)—C(12)	1.500 (3)
C(11)—C(16)	1.504 (3)	C(12)—F	1.383 (3)
O(1)—P—O(2)	105.6 (1)	O(1)—P—O(3)	99.7 (1)
O(2)—P—O(3)	99.8 (1)	O(1)—P—O(4)	116.5 (1)
O(2)—P—O(4)	115.0 (1)	O(3)—P—O(4)	117.8 (1)
P—O(1)—C(11)	122.9 (1)	P—O(2)—C(21)	122.3 (1)
P—O(3)—C(31)	120.8 (1)	O(1)—C(11)—C(12)	109.0 (2)
O(1)—C(11)—C(16)	108.4 (2)	C(12)—C(11)—C(16)	110.9 (2)
C(11)—C(12)—F	108.6 (2)	C(11)—C(12)—C(13)	111.2 (2)
F—C(12)—C(13)	110.0 (2)		
Compound (3)			
S—O(1)	1.583 (2)	S—O(2)	1.428 (2)
S—O(3)	1.416 (2)	S—C(11)	1.755 (3)
O(1)—C(1)	1.466 (3)	C(1)—C(2)	1.504 (4)
C(1)—C(6)	1.503 (4)	C(2)—F	1.392 (3)
O(1)—S—O(2)	109.5 (1)	O(1)—S—O(3)	103.4 (1)
O(2)—S—O(3)	120.1 (1)	O(1)—S—C(11)	103.6 (1)
O(2)—S—C(11)	109.0 (1)	O(3)—S—C(11)	110.0 (1)
S—O(1)—C(1)	119.5 (2)	O(1)—C(1)—C(2)	106.5 (2)
O(1)—C(1)—C(6)	110.0 (2)	C(2)—C(1)—C(6)	110.5 (2)
C(1)—C(2)—F	108.8 (2)	C(1)—C(2)—C(3)	111.9 (2)
F—C(2)—C(3)	110.0 (2)		

($\pm h\ -k\ \pm l$ and some $-h\ +k\ +l$), 2626 unique (R_{int} 0.017), 2098 > $4\sigma(F)$, index ranges h 0 to 13, k 0 to 18, l −9 to 9. Cell constants from 42 reflections in the 2θ range 20–23°. R 0.053, wR 0.070 for 190 parameters; S 2.6; max. Δ/σ 0.015; max. $\Delta\rho$ +0.50, −0.26 e Å^{-3}. The residual electron density is larger than usual and may indicate a marginal degree of disorder.

Discussion. Final atom coordinates for (1)–(3) are given in Tables 1–3 and derived parameters in Table 4. Plots of (1)–(3), showing the atom-numbering schemes, appear as Figs. 1–3.* There are no non-bonded contacts < 3.3 Å in any of the three structures.

Apart from a possible marginal indication for (3), the equatorial F atom shows no disorder in any of the three compounds examined in this paper, in marked contrast to the six axial derivatives described in the two following papers (Jones, Kirby & Parker, 1992*d*,*e*), all of which show substantial positional disorder. The geometry of the C—F bond is fixed *gauche* to C—O by the chair conformation of the ring [dihedral angle between 60.7 and 63.0° for the three compounds (1)–(3)], and the geometries and conformations of the esterifying groups are normal in each case. (We have measured sufficient carboxylic, phosphate and sulfonate esters in this series of investigations to make extensive internal comparisons.) So we discuss here only the point of primary interest for this investigation, the length of the C—O*X* bond.

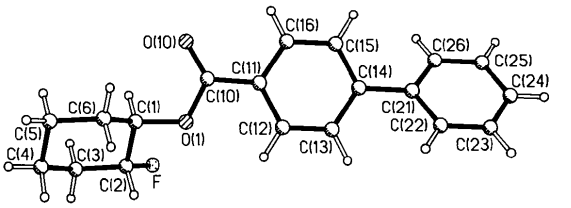

Fig. 1. Molecular structure of (1), showing the atom-numbering scheme.

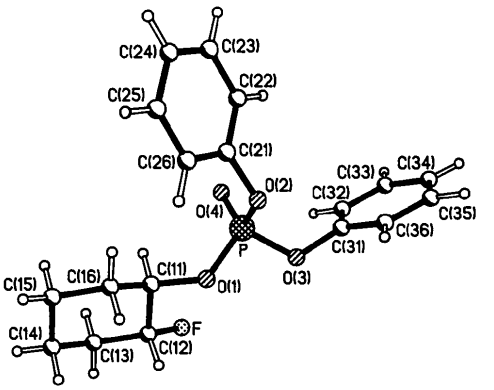

Fig. 2. Molecular structure of (2), showing the atom-numbering scheme.

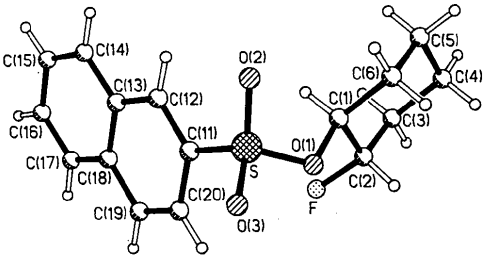

Fig. 3. Molecular structure of (3), showing the atom-numbering scheme.

* 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 54758 (53 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0058]

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.

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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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