

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, 1992a,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—OX bond lengths of two homogeneous series of compounds of fixed conformation.

We thank the Fonds der Chemischen Industrie for support.

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

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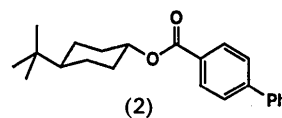
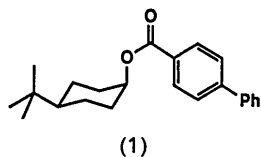
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Abstract. *cis*-4-*tert*-Butylcyclohexyl 4-phenylbenzoate, (1), C₂₃H₂₈O₂, *M_r* = 336.48, monoclinic, *P*2₁/*n*, *a* = 6.376 (2), *b* = 14.317 (7), *c* = 21.792 (8) Å, β = 92.64 (3)°, *V* = 1987 Å³, *Z* = 4, *D_x* = 1.125 Mg m⁻³, λ (Mo *K* α) = 0.71069 Å, μ = 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), C₂₃H₂₈O₂, *M_r* = 336.48, monoclinic, *P*2₁/*n*, *a* = 12.951 (2), *b* = 10.836 (2), *c* = 14.022 (2) Å, β = 102.66 (2)°, *V* = 1920.1 Å³, *Z* = 4, *D_x* = 1.164 Mg m⁻³, λ (Mo *K* α) = 0.71069 Å, μ = 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, 1992a,b; Jones, Kirby & Parker, 1992) has shown that the effect on the length of the C—OX 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).



Experimental. *cis*-4-*tert*-Butylcyclohexyl 4-phenylbenzoate (1) was obtained by esterification, as described below for the *trans* isomer, of the mixture of the *cis* alcohol and *trans*-3-*tert*-butylcyclohexanol obtained by reduction of the *cis* and *trans* mixture of 3,4-epoxides with lithium aluminium hydride. [To a stirred solution of 4-*tert*-butylcyclohexene (45.5 g, 0.33 mol) in CH_2Cl_2 was added NaHCO_3 (40 g), then 85% *m*-chloroperbenzoic acid (45 g, 0.33 mol). After 1.5 h the solution was extracted in turn with Na_2SO_3 , NaHCO_3 and saturated NaCl solutions, evaporated, and the product distilled to give a mixture of *cis*- and *trans*-epoxides, b.p. 341–343 K/8 mm Hg. 1.3 g (8 mmol) of this mixture was dissolved in tetrahydrofuran and reduced with LiAlH_4 (0.38 g, 10 mmol). Addition of water, removal of THF *in vacuo* and extraction with ether gave the mixture of alcohols as needles (88%, m.p. 325–332 K.)] The mixed esters (72%) were separated by HPLC (eluant 1:1 CH_2Cl_2 –hexane), to give the *trans*-3-*tert*-butyl isomer described in the following paper, and *cis*-4-*tert*-butylcyclohexyl 4-phenylbenzoate, R_T 16 min, m.p. 352–357 K. Single crystals were grown as colourless blocks from pentane.

trans-4-*tert*-Butylcyclohexyl 4-phenylbenzoate (2). 4-*tert*-Butylcyclohexanols were obtained as a *cis/trans* mixture from Aldrich. A solution in CH_2Cl_2 of biphenyl-4-carboxylic acid (0.48 g, 2.4 mmol), the mixed alcohols (2.6 mmol), 1,3-dicyclohexylcarbodiimide (0.53 g, 2.6 mmol) and 4-dimethylaminopyridine (30 mg, 0.2 mmol), was stirred at room temperature for 2 h. It was filtered, extracted with water (3 × 50 ml), 5% acetic acid (3 × 50 ml), then water (3 × 50 ml) again, dried over MgSO_4 , and the solvent removed *in vacuo*. The *trans* isomer crystallized selectively from CH_2Cl_2 –pentane as needles, m.p. 388–389 K. Single crystals were obtained as colourless prisms by liquid diffusion of pentane into a solution in diethyl ether.

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 $1.0 \times 0.8 \times 0.7$ [$1.0 \times 0.4 \times 0.2$] mm was mounted in a glass capillary. 3828 [4423] reflections ($-h + k \pm l$ and some $+h$ equivalents [$\pm h + k + l$ and some $-l$ equivalents]) were collected on a Siemens R3 [Stoe–Siemens] diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{\text{max}} 50^\circ$). Three check reflections showed no significant intensity change. No absorption correction was applied. Merging equivalents gave 3499 [3363] unique reflections ($R_{\text{int}} 0.028$ [0.029], index ranges after merging $h 0$ to 7 [0 to 14], $k 0$ to 17 [0 to 12], $l -25$ to 25 [-16 to 16]), of which 2534 [2351] with $F > 4\sigma(F)$ were used for all calculations (program system Siemens *SHELXTL-Plus*; Sheldrick, 1990). The

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (1)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
C(1)	4307 (3)	6631 (1)	2996 (1)	68 (1)
O(1)	5420 (2)	7426 (1)	2976 (1)	65 (1)
O(2)	2645 (2)	6517 (1)	2720 (1)	100 (1)
C(11)	4558 (3)	8172 (1)	2580 (1)	73 (1)
C(12)	2923 (3)	8710 (1)	2910 (1)	78 (1)
C(13)	3841 (3)	9291 (1)	3439 (1)	71 (1)
C(14)	5569 (2)	9950 (1)	3241 (1)	61 (1)
C(15)	7261 (2)	9359 (1)	2957 (1)	67 (1)
C(16)	6401 (3)	8781 (1)	2421 (1)	78 (1)
C(17)	6397 (3)	10644 (1)	3738 (1)	73 (1)
C(18)	4581 (4)	11225 (2)	3969 (1)	114 (1)
C(19)	7950 (4)	11321 (2)	3463 (1)	112 (1)
C(20)	7517 (4)	10149 (2)	4283 (1)	109 (1)
C(21)	5331 (2)	5915 (1)	3400 (1)	57 (1)
C(22)	7370 (2)	5996 (1)	3644 (1)	61 (1)
C(23)	8213 (2)	5316 (1)	4032 (1)	60 (1)
C(24)	7044 (2)	4537 (1)	4188 (1)	54 (1)
C(25)	5010 (2)	4461 (1)	3933 (1)	63 (1)
C(26)	4169 (2)	5134 (1)	3550 (1)	65 (1)
C(31)	7910 (2)	3805 (1)	4609 (1)	57 (1)
C(32)	6722 (3)	3463 (1)	5083 (1)	70 (1)
C(33)	7498 (4)	2766 (1)	5466 (1)	87 (1)
C(34)	9436 (4)	2391 (1)	5386 (1)	92 (1)
C(35)	10636 (3)	2717 (1)	4923 (1)	91 (1)
C(36)	9872 (3)	3422 (1)	4537 (1)	74 (1)

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

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) for (1)

C(1)—O(1)	1.343 (2)	C(1)—O(2)	1.205 (2)
C(1)—C(21)	1.483 (2)	O(1)—C(11)	1.464 (2)
C(11)—C(12)	1.505 (2)	C(11)—C(16)	1.516 (3)
O(1)—C(1)—O(2)	123.6 (1)	O(1)—C(1)—C(21)	112.7 (1)
O(2)—C(1)—C(21)	123.7 (2)	C(1)—O(1)—C(11)	116.9 (1)
O(1)—C(11)—C(12)	110.0 (1)	O(1)—C(11)—C(16)	106.3 (1)
C(12)—C(11)—C(16)	112.2 (1)	C(11)—C(12)—C(13)	113.1 (1)

orientation matrix [cell constants] was [were] refined from diffractometer [$\pm \omega$] angles of 48 [44] reflections in the range $2\theta 20$ – 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 final R was 0.041 [0.056], with wR 0.052 [0.060]. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$, with g 0.00025 [0.0003]. 235 [226] parameters; S 2.1 [1.9]; max. Δ/σ 0.086 [0.001]; max. $\Delta\rho + 0.11$, -0.15 [$+0.16$, -0.22] e \AA^{-3} .

Discussion. Final atom coordinates for (1) and (2) are given in Tables 1 and 3,* and derived parameters in Tables 2 and 4, respectively. Plots of (1) and (2),

* 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 54755 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0055]

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} [*]
C(1)	6903 (2)	3189 (2)	2943 (2)	58 (1)
O(1)	6296 (1)	2173 (1)	2852 (1)	61 (1)
O(2)	6554 (1)	4213 (2)	2804 (1)	84 (1)
C(11)	5152 (2)	2354 (2)	2607 (2)	55 (1)
C(12)	4662 (2)	1286 (2)	3031 (2)	62 (1)
C(13)	3461 (2)	1393 (2)	2773 (2)	62 (1)
C(14)	3010 (2)	1475 (2)	1674 (2)	53 (1)
C(15)	3554 (2)	2529 (2)	1251 (2)	60 (1)
C(16)	4756 (2)	2431 (2)	1517 (2)	60 (1)
C(17)	1785 (2)	1522 (2)	1390 (2)	62 (1)
C(18)	1406 (2)	1530 (3)	279 (2)	86 (1)
C(19)	1316 (2)	384 (3)	1779 (2)	93 (1)
C(20)	1351 (2)	2663 (3)	1809 (2)	88 (1)
C(21)	8042 (2)	2890 (2)	3288 (2)	52 (1)
C(22)	8418 (2)	1704 (2)	3367 (2)	71 (1)
C(23)	9468 (2)	1465 (2)	3760 (2)	74 (1)
C(24)	10183 (2)	2388 (2)	4104 (2)	51 (1)
C(25)	9802 (2)	3581 (2)	3988 (2)	67 (1)
C(26)	8754 (2)	3834 (2)	3586 (2)	70 (1)
C(31)	11293 (2)	2109 (2)	4606 (2)	54 (1)
C(32)	11659 (2)	921 (3)	4741 (2)	81 (1)
C(33)	12670 (2)	647 (3)	5238 (2)	97 (1)
C(34)	13347 (2)	1558 (3)	5619 (2)	91 (1)
C(35)	13011 (2)	2746 (3)	5502 (3)	115 (2)
C(36)	12001 (2)	3018 (3)	4996 (2)	97 (1)

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

Table 4. Selected bond lengths (\AA) and angles ($^\circ$) for (2)

C(1)—O(1)	1.343 (3)	C(1)—O(2)	1.198 (3)
C(1)—C(21)	1.484 (3)	O(1)—C(11)	1.458 (2)
C(11)—C(12)	1.505 (3)	C(11)—C(16)	1.504 (3)
O(1)—C(1)—O(2)	123.4 (2)	O(1)—C(1)—C(21)	111.8 (2)
O(2)—C(1)—C(21)	124.6 (2)	C(1)—O(1)—C(11)	117.1 (2)
O(1)—C(11)—C(12)	107.3 (2)	O(1)—C(11)—C(16)	110.4 (2)
C(12)—C(11)—C(16)	111.4 (2)	C(11)—C(12)—C(13)	110.2 (2)

showing the atom-numbering schemes, appear as Figs. 1 and 2. The packing diagram of (2) shows that the biphenyl groups are arranged approximately parallel to each other. The shortest non-bonded distance in (2) (excluding H atoms; symmetry operator refers to the second atom) is C(22)⋯O(2) 3.16 \AA ($1.5 - x, -0.5 + y, 0.5 - z$). In (1) there are no such contacts $< 3.3 \text{\AA}$.

The mean value for the length of the C—O bond of a secondary alkyl ester, taken from a published survey of the Cambridge Structural Database (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), is 1.460 (10) \AA . An identical value [1.460 (2) \AA] was found for a smaller set of the same data screened for potential electronic effects (Allen & Kirby, 1984). For all esters of cyclohexanols the mean database value is slightly higher (1.467 \AA). Furthermore, it appears to be conformation dependent. For the 14 equatorial compounds we find a mean value of 1.465 \AA , but for the three axial esters the mean is

1.488 \AA . The difference is not statistically significant, but raises the possibility of a conformation dependence of bond length, as observed in acetal structures, which needs to be addressed.

Our new data for both (1) and (2), and the related structure discussed in the following paper, agree with the mean value derived for all secondary esters, and thus are not consistent with the axial C—O ester bond being substantially longer. The length of the equatorial C—O ester bond in (2) is 1.458 (2) \AA , identical with the database value [1.460 (2) \AA] quoted above. We therefore take this as a standard value for equatorial (4-phenylbenzoate) esters of cyclohexanols. [We expect the length of this bond to depend on the strength of the carboxylic acid involved (Jones & Kirby, 1979, 1984).]

The length of the axial C—O ester bond in (1) is 1.464 (2) \AA , not significantly different from the value for the equatorial compound (2). The geometry and conformations of the ester group are also almost identical in the two isomers, though the biphenyl unit, unusually, is almost planar (torsion angle *ca* 1 $^\circ$) in (2). In (1) the two ring planes adopt a more usual arrangement, with the torsion angle between them 47 $^\circ$. (For five other 4-phenylbenzoate esters in this series of papers we find this torsion angle to be

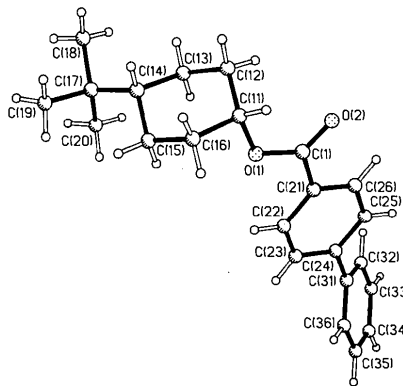


Fig. 1. Molecular structure of (1), showing the atom-numbering scheme.

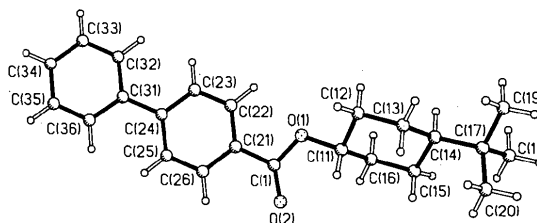


Fig. 2. Molecular structure of (2), showing the atom-numbering scheme.

$33 \pm 10^\circ$). We have no reason to expect the length of the C—O ester bond to be affected by changes in this torsion angle (any effect would be to exaggerate the difference in C—O bond length) so we have a reasonably reliable value for the length of this bond in a simple axial cyclohexyl ester of 4-phenylbenzoic acid, or other acid with a similar pK_a . In the following paper we report the structure of a second axial ester which gives a closely similar result.

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

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Bond Length and Reactivity. Structure of the 4-Phenylbenzoate Ester of *trans*-3-*tert*-Butylcyclohexanol

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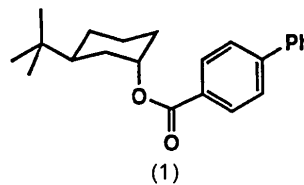
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Abstract. *trans*-3-*tert*-Butylcyclohexyl 4-phenylbenzoate, $C_{23}H_{28}O_2$, $M_r = 336.48$, monoclinic, $P2_1/c$, $a = 13.921$ (2), $b = 11.408$ (3), $c = 12.591$ (3) Å, $\beta = 100.61$ (2)°, $V = 1965.4$ Å³, $Z = 4$, $D_x = 1.137$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.07$ mm⁻¹, $F(000) = 728$, $T = 293$ K. Final $R = 0.049$ for 2516 unique observed reflections. The axial ester C—O bond length is 1.461 (2) Å, almost equal to that in the isomer *cis*-4-*tert*-butylcyclohexyl 4-phenylbenzoate described in the previous paper. This allows accurate definition of the length of the axial ester bond in the absence of strongly electron-withdrawing substituents.

Introduction. This is the second in a series of papers attempting to define standard C—O bond lengths for cyclohexyl esters. In the previous paper (Jones, Kirby & Parker, 1992) we were able to define this parameter for esters of equatorial cyclohexanols with good precision, and reported an accurate value for the axial C—O ester bond length in *cis*-4-*tert*-

butylcyclohexyl 4-phenylbenzoate. We report here the structure of an axial isomer, *trans*-3-*tert*-butylcyclohexyl 4-phenylbenzoate (1).



Experimental. The preparation of *trans*-3-*tert*-butylcyclohexyl 4-phenylbenzoate was described in the previous paper (Jones, Kirby & Parker, 1992). Separation from the 4-*tert*-butyl isomer by HPLC (R_T 18 min) gave crystals, m.p. 361–363 K. Single crystals (as colourless prisms and tablets) were grown by slow evaporation of a solution in petroleum ether, b.p. 313–333 K.

A crystal $1.0 \times 0.8 \times 0.25$ (cut from a larger tablet) was mounted on a glass fibre. 5011 reflections ($+h$

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