33 ± 10°). 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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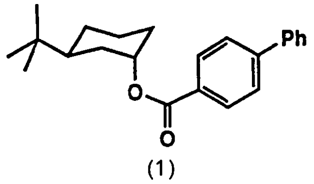
Abstract. *trans*-3-*tert*-Butylcyclohexyl 4-phenylbenzoate, $C_{23}H_{28}O_2$, $M_r = 336.48$, monoclinic, $P2_1/c$, $a = 13.921$ (2), $b = 11.408$ (3), $c = 12.591$ (3) Å, $\beta = 100.61$ (2)°, $V = 1965.4$ Å^3, $Z = 4$, $D_x = 1.137$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.07$ mm^{-1}, $F(000) = 728$, $T = 293$ 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).



(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 × 0.8 × 0.25 (cut from a larger tablet) was mounted on a glass fibre. 5011 reflections (+*h*

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$+k \pm l$ and some $-h$ equivalents) were collected on a Stoe–Siemens diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{\max}$ 50°). Three check reflections increased slightly in intensity, which may be due to decreased extinction on irradiation; a corresponding correction was applied. Merging equivalents gave 3458 uniqe reflections (R_{int} 0.024, index ranges after merging h 0–16, k 0–13, l −14 to 14), of which 2516 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens *SHELXTL-Plus*; Sheldrick, 1990). The cell constants were refined from $\pm\omega$ angles of 48 reflections in the range 2θ 20–24°. 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 0.049, with wR 0.055. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003F^2$. 226 parameters; S 1.8; max. Δ/σ 0.002; max. $\Delta\rho$ +0.13, −0.19 e Å^{-3}.

Discussion. Final atom coordinates for (1) are given in Table 1,* and derived parameters in Table 2. A plot showing the atom-numbering scheme appears as Fig. 1 and the 'herringbone' packing adopted by (1) is shown in Fig. 2. The only non-bonded distance (excluding H atoms) < 3.3 Å is C(23)···O(2) 3.24 Å (O at $1-x$, $1-y$, $1-z$). The dihedral angle between the rings of the biphenyl moiety is 34°.

The ester adopts the expected conformation, with the *tert*-butyl group equatorial and the ester group axial. The geometry of the ester group is closely similar to that of the esters described in the previous paper in this series (Jones, Kirby & Parker, 1992), and the length of the C—O ester bond is 1.461 (2) Å. This is identical, within experimental error, with the length of the corresponding bond in the 3-*tert*-butyl isomer and with the mean value for all esters of secondary alcohols obtained from database searches (Jones, Kirby & Parker, 1992). We take a best value of 1.462 (2) Å for the length of the C—O ester bond in a simple axial cyclohexyl ester of 4-phenylbenzoic acid, or other acid with a similar pK_a. Note that for these esters at least there is no significant axial/equatorial difference in C—O ester bond length: all the available data are consistent with a value of 1.462 (4) Å.

In the following paper we present data for axial and equatorial cyclohexyl esters of sulfonic acids.

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

	x	y	z	U_{eq}*
C(1)	6167 (1)	3467 (2)	8273 (2)	64 (1)
O(1)	6641 (1)	2554 (1)	8792 (1)	66 (1)
O(2)	6244 (1)	4452 (1)	8622 (1)	95 (1)
C(11)	7285 (1)	2770 (2)	9828 (2)	67 (1)
C(12)	8275 (1)	3183 (2)	9636 (2)	65 (1)
C(13)	8813 (1)	2259 (2)	9088 (1)	56 (1)
C(14)	8865 (1)	1120 (2)	9734 (2)	69 (1)
C(15)	7866 (1)	699 (2)	9898 (2)	71 (1)
C(16)	7336 (2)	1629 (2)	10427 (2)	76 (1)
C(17)	9808 (1)	2669 (2)	8835 (2)	65 (1)
C(18)	9687 (2)	3800 (2)	8187 (2)	96 (1)
C(19)	10560 (2)	2866 (3)	9852 (2)	106 (1)
C(20)	10193 (2)	1738 (3)	8144 (2)	108 (1)
C(21)	5548 (1)	3133 (2)	7236 (2)	56 (1)
C(22)	5543 (1)	2004 (2)	6816 (2)	57 (1)
C(23)	4960 (1)	1740 (2)	5843 (2)	56 (1)
C(24)	4363 (1)	2578 (2)	5247 (2)	56 (1)
C(25)	4385 (1)	3707 (2)	5674 (2)	66 (1)
C(26)	4963 (1)	3976 (2)	6649 (2)	64 (1)
C(31)	3712 (1)	2278 (2)	4218 (2)	59 (1)
C(32)	3503 (2)	3075 (2)	3366 (2)	75 (1)
C(33)	2902 (2)	2783 (3)	2412 (2)	88 (1)
C(34)	2489 (2)	1697 (3)	2277 (2)	88 (1)
C(35)	2677 (2)	896 (2)	3102 (2)	83 (1)
C(36)	3281 (1)	1176 (2)	4062 (2)	67 (1)

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

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

C(1)—O(1)	1.337 (2)	C(1)—O(2)	1.205 (3)
C(1)—C(21)	1.475 (3)	O(1)—C(11)	1.461 (2)
C(11)—C(12)	1.516 (3)	C(11)—C(16)	1.499 (3)
O(1)—C(1)—O(2)	123.0 (2)	O(1)—C(1)—C(21)	112.8 (2)
O(2)—C(1)—C(21)	124.2 (2)	C(1)—O(1)—C(11)	118.1 (1)
O(1)—C(11)—C(12)	109.7 (2)	O(1)—C(11)—C(16)	105.5 (2)
C(12)—C(11)—C(16)	113.0 (2)	C(11)—C(12)—C(13)	113.1 (2)

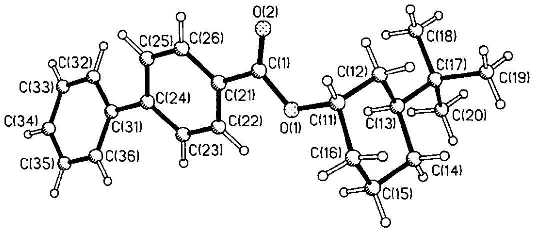

Fig. 1. Molecular structure of (1), showing the atom-numbering scheme.

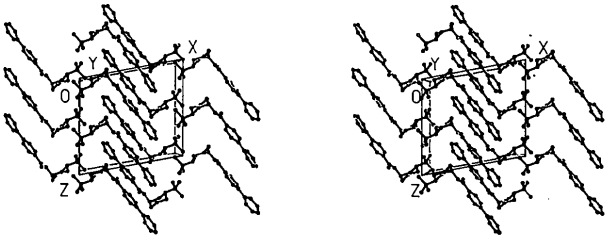

Fig. 2. Molecular packing of (1).

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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 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54756 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0056]

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

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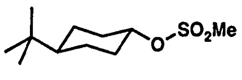
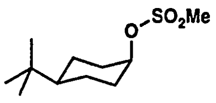
Abstract. *trans*-4-*tert*-Butylcyclohexyl methanesulfonate, (1), $C_{11}H_{22}O_3S$, $M_r = 234.35$, orthorhombic, $Pca2_1$, $a = 9.424$ (5), $b = 17.177$ (9), $c = 8.321$ (3) Å, $V = 1347$ Å^3, $Z = 4$, $D_x = 1.156$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.22$ mm^{-1}, $F(000) = 512$, $T = 293$ K. Final $R = 0.070$ for 1245 unique observed reflections. *cis*-4-*tert*-Butylcyclohexyl methanesulfonate, (2), $C_{11}H_{22}O_3S$, $M_r = 234.35$, monoclinic, $P2_1/c$, $a = 21.081$ (3), $b = 6.0693$ (6), $c = 10.3058$ (16) Å, $\beta = 94.944$ (12)°, $V = 1313.7$ Å^3, $Z = 4$, $D_x = 1.185$ Mg m^{-3}, $\mu = 0.22$ mm^{-1}, $F(000) = 512$, $T = 293$ K. Final $R = 0.050$ for 2476 unique observed reflections. The compounds are axial and equatorial isomers, with similar geometries around the sulfonate ester group. In particular, the ester C—O bond lengths [1.485 (9) Å for (1) and 1.480 (3) Å for (2)] are almost equal, and inconsistent with suggestions that there are significant differences in the lengths of axial and equatorial isomers. Standard C—O bond lengths for cyclohexanol derivatives R—OX, which may be expected to hold for all derivatives of simple secondary alcohols, are defined in terms of the pK_a of the leaving-group acid OX, using a combination of mean database values and new data presented in this and earlier papers in this series.

Introduction. This is the third in a series of papers attempting to define standard C—O bond lengths for cyclohexyl esters. In the two previous papers (Jones, Kirby & Parker, 1992*a*,*b*) we were able to define this parameter for carboxylic esters of equatorial cyclohexanols with good precision, and reported accurate values for the axial C—O ester bond length in two *tert*-butylcyclohexyl 4-phenylbenzoates that were not significantly different from the best value for the equatorial system. We report here the structures of a second pair of axial and equatorial isomers, *trans*- and *cis*-4-*tert*-butylcyclohexyl methanesulfonate (1) and (2).



(1)



(2)

Experimental. *trans*-4-*tert*-Butylcyclohexyl methanesulfonate (1) was prepared from the commercial mixture of 4-*tert*-butylcyclohexanols by the general method for sulfonate esters described previously (Kirby, Parker & Raithby, 1992). Recrystallization from CH_2Cl_2 gave the mixed methanesulfonates as prisms (68%). Repeated crystallization from CH_2Cl_2–hexane gave the pure *trans*-mesylate (1), m.p. 341–344 K (lit. 347–348 K; Noyce, Johnson & Weinstein, 1969). Single crystals were grown in the form of colourless prisms by the liquid diffusion technique, also using CH_2Cl_2–hexane.

cis-4-*tert*-Butylcyclohexyl methanesulfonate (2) was prepared in similar fashion from the mixture of 3- and 4-*tert*-butylcyclohexanols obtained by reduction of the mixed epoxides, as described previously (Jones, Kirby & Parker, 1992*a*). Recrystallization

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