

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

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

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(Received 14 January 1991; accepted 14 October 1991)

**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<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.156$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 0.22$  mm<sup>-1</sup>,  $F(000) = 512$ ,  $T = 293$  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<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.185$  Mg m<sup>-3</sup>,  $\mu = 0.22$  mm<sup>-1</sup>,  $F(000) = 512$ ,  $T = 293$  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 cyclo-

hexanols 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).



**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

from CH<sub>2</sub>Cl<sub>2</sub>-hexane gave the mixture of mesylates (83%) as platelets. Repeated recrystallization from the same solvent gave the title compound as platelets, m.p. 363–365.3 K. Single crystals were obtained as colourless prisms by the liquid diffusion technique, also using CH<sub>2</sub>Cl<sub>2</sub>-hexane.

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 0.7 × 0.35 × 0.3 [1.0 × 0.6 × 0.5] mm was mounted in a glass capillary. 2119 [6030] reflections (+*h* +*k* +*l* and some −*h* −*k* −*l* [ $\pm h$  +*k*  $\pm l$ ]) were collected on a Stoe-Siemens [Siemens R3] diffractometer using monochromated Mo *K*α radiation (2θ<sub>max</sub> 50 [55]°). Three check reflections showed no significant intensity change. No absorption correction was applied. Merging equivalents gave 1833 [3025] unique reflections (*R*<sub>int</sub> 0.028 [0.017]), index ranges after merging *h* 0 to 11 [0 to 27], *k* 0 to 20 [0 to 7], *l* −4 to 9 [−13 to 13], of which 1245 [2476] with *F* > 4σ(*F*) were used for all calculations (program system Siemens *SHELXTL-Plus*; Sheldrick, 1990). The cell constants were refined from ±*w* angles of 48 [42] reflections in the range 2θ 20–23°. 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. An η refinement (Rogers, 1981) for (1) was inconclusive, with η = +1.4 (4). The final *R* was 0.070 [0.050], with *wR* 0.075 [0.064]. The poor *R* value of (1) is probably attributable to its wide reflection profiles. The weighting scheme was *w*<sup>−1</sup> = σ<sup>2</sup>(*F*) + *gF*<sup>2</sup>, with *g* 0.0007 [0.0002]. 135 [136] parameters; *S* 1.8 [3.1]; max. Δ/σ 0.003 [0.001]; max. Δρ +0.41, −0.45 [+0.19, −0.40] e Å<sup>−3</sup>.

**Discussion.** Final atom coordinates for (1) and (2) are given in Tables 1 and 3,\* and selected derived parameters in Tables 2 and 4. Plots of (1) and (2), showing the atom-numbering schemes, appear as Figs. 1 and 2.

The mean value for the length of the C—O bond of an alkyl sulfonate ester, taken from a published survey of the Cambridge Structural Database (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), is 1.465 (14) Å. For secondary alkyl sulfonates this rises to 1.475 Å, and for a data set restricted to cyclohexyl derivatives we find a database mean of

Table 1. Atomic coordinates (× 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for (1)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>*</sup>
S(1)	5667 (2)	5937 (1)	2000	64 (1)
O(1)	4667 (5)	6239 (2)	3351 (8)	68 (2)
O(2)	6392 (5)	6560 (3)	1268 (7)	78 (2)
O(3)	4774 (6)	5464 (3)	1026 (8)	95 (2)
C(1)	5177 (7)	6854 (3)	4465 (12)	64 (3)
C(2)	4702 (10)	6658 (4)	6105 (11)	92 (4)
C(3)	5117 (9)	7285 (4)	7299 (10)	83 (3)
C(4)	4557 (6)	8080 (3)	6825 (11)	53 (2)
C(5)	4974 (11)	8244 (4)	5129 (11)	92 (3)
C(6)	4563 (10)	7606 (4)	3948 (11)	93 (3)
C(7)	4910 (7)	8735 (4)	8060 (10)	64 (3)
C(8)	4488 (14)	8530 (5)	9712 (13)	136 (5)
C(9)	4073 (18)	9463 (5)	7599 (16)	193 (8)
C(10)	6468 (11)	8928 (7)	8075 (19)	193 (7)
C(11)	6886 (8)	5346 (3)	2991 (11)	82 (3)

\* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

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

S(1)—O(1)	1.556 (6)	S(1)—O(2)	1.409 (5)
S(1)—O(3)	1.424 (6)	S(1)—C(11)	1.741 (8)
O(1)—C(1)	1.485 (9)	C(1)—C(2)	1.476 (13)
O(1)—S(1)—O(2)	110.6 (3)	O(1)—S(1)—O(3)	104.1 (3)
O(2)—S(1)—O(3)	118.3 (3)	O(1)—S(1)—C(11)	104.6 (4)
O(2)—S(1)—C(11)	109.2 (3)	O(3)—S(1)—C(11)	109.1 (3)
S(1)—O(1)—C(1)	119.5 (4)	O(1)—C(1)—C(2)	108.5 (5)
O(1)—C(1)—C(6)	108.2 (7)	C(2)—C(1)—C(6)	110.5 (7)

Table 3. Atomic coordinates (× 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for (2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>*</sup>
S	923.8 (2)	5025.5 (8)	4321.4 (4)	61 (1)
O(1)	1603.0 (6)	5223 (2)	3829 (1)	69 (1)
O(2)	1000.7 (7)	5629 (3)	5648 (1)	91 (1)
O(3)	658.6 (7)	2922 (3)	3998 (2)	93 (1)
C(1)	1752 (1)	4070 (4)	2627 (2)	70 (1)
C(2)	2158 (1)	5638 (4)	1923 (2)	75 (1)
C(3)	2799 (1)	6052 (3)	2671 (2)	60 (1)
C(4)	3163 (1)	3920 (3)	3005 (1)	45 (1)
C(5)	2740 (1)	2405 (3)	3744 (2)	60 (1)
C(6)	2102 (1)	1977 (3)	2994 (2)	76 (1)
C(7)	3839 (1)	4265 (3)	3688 (2)	47 (1)
C(8)	3818 (1)	5494 (3)	4980 (2)	66 (1)
C(9)	4249 (1)	5595 (4)	2813 (2)	73 (1)
C(10)	4168 (1)	2045 (3)	3949 (2)	72 (1)
C(11)	487 (1)	7027 (4)	3439 (3)	86 (1)

\* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

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

S—O(1)	1.564 (1)	S—O(2)	1.411 (1)
S—O(3)	1.422 (2)	S—C(11)	1.734 (3)
O(1)—C(1)	1.480 (3)	C(1)—C(2)	1.507 (3)
O(1)—S—O(2)	105.2 (1)	O(1)—S—O(3)	110.2 (1)
O(2)—S—O(3)	118.1 (1)	O(1)—S—C(11)	103.7 (1)
O(2)—S—C(11)	109.7 (1)	O(3)—S—C(11)	109.0 (1)
S—O(1)—C(1)	120.1 (1)	O(1)—C(1)—C(2)	105.9 (2)
O(1)—C(1)—C(6)	108.9 (2)	C(2)—C(1)—C(6)	111.6 (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 54757 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0057]

1.480 Å. For the subset of 10 equatorial compounds the mean C—O bond length is 1.483 Å, and for 11 axial esters the mean is 1.484 Å.

The database values posed a problem, because they suggested a substantial difference between axial and equatorial carboxylic esters (Jones, Kirby & Parker, 1992*b*), but not for sulfonates. However, closer inspection of the individual data showed the data for sulfonates to be very variable. A set of simple axial and equatorial cyclohexyl tosylates measured by James *et al.* in the 1970's is particularly relevant to this work (James, 1973*a,b*; James & McConnell, 1971; James & Grainger, 1972; James & Moore, 1975; Johnson, Cheer, Schaefer, James & Moore, 1972; Johnson, Schaefer, James & McConnell, 1972), but the data are not good enough to decide whether the C—O bond lengths of axial and equatorial derivatives differ.

Our new data for mesylates (1) and (2) are also not as accurate as we would like; but the C—O bond lengths agree with the mean values for axial and equatorial tosylates cited above, and are not significantly different for the two isomers. The conformations around the sulfonate group are similar in the two compounds, and the C—O bond lengths are 1.485 (9) and 1.480 (3) Å for the equatorial and axial isomers, respectively. [The  $pK_a$ 's of *p*-toluene- and methanesulfonic acid are thought to differ by less than one unit (Stewart, 1985), so we can safely ignore the difference of leaving group between the mesylates and the tosylates.]

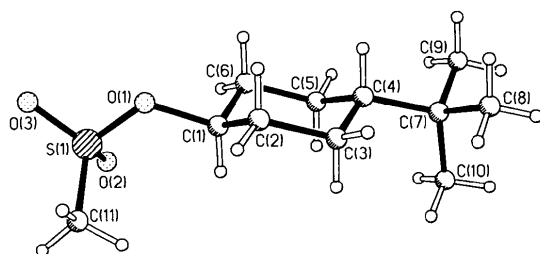


Fig. 1. Molecular structure of (1), showing the atom-numbering scheme.

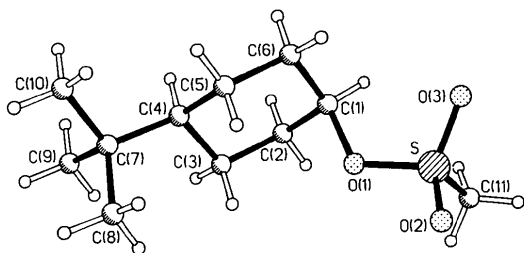


Fig. 2. Molecular structure of (2), showing the atom-numbering scheme.

We conclude that there is no good evidence for a significant difference in C—O bond length between axial and equatorial cyclohexyl sulfonate esters, and that a value of 1.483 (4) Å is in agreement with the best data. {We note that the mean C—O bond length for three 2-hydroxycyclohexyl arenesulfonates that we measured recently is marginally shorter than this [1.477 (2) Å; Jones, Edwards & Kirby, 1989].}

Our best values for cyclohexyl carboxylate and sulfonate esters, obtained in this and the previous papers of this series (Jones, Kirby & Parker, 1992*a,b*) turn out not to differ from mean database values. Combined with other mean database values (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) for secondary alkyl and aryl ethers, they allow us to define the linear relationship (correlation coefficient 0.999 for four points) for derivatives  $R-OX$  of cyclohexanol, in terms of the  $pK_a$  of the conjugate acid of  $HOX$ :

$$\text{Bond length (\AA)} = 1.475 - 2.90 \times 10^{-3} pK_{HOX}.$$

This expression should hold for derivatives of all secondary alcohols without electronegative substituents.

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

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