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Bond Length and Reactivity. Structure of 2-Phenylethyl *p*-Toluenesulfonate

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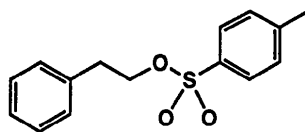
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Abstract. C₁₅H₁₆O₃S, *M_r* = 276.35, triclinic, *P* $\bar{1}$, *a* = 7.353 (1), *b* = 8.136 (1), *c* = 24.307 (4) Å, α = 94.44 (1), β = 89.81 (1), γ = 105.51 (1)°, *V* = 1396.8 (4) Å³, *Z* = 4, *D_x* = 1.314 Mg m⁻³, λ (Cu *K* α) = 1.54178 Å, μ = 2.02 mm⁻¹, *F*(000) = 584, *T* = 293 K. Final *R* = 0.059 for 3401 observed reflections [*F* > 4 σ (*F*)] and 355 parameters. The asymmetric unit contains two independent but structurally similar molecules. Each molecule adopts a folded conformation in which the two aromatic rings lie over each other, with a centroid-to-centroid distance of 4.05 Å in molecule (1) and 3.87 Å in molecule (2). The bond parameters within each molecule do not deviate significantly from expected values, but the torsion angles about the PhCH₂—CH₂ bond (C_{ar}—C—O) of 71.7 (3) and 68.4 (3)° for the two molecules show that the *gauche* conformation is preferred. A best value of 1.462 (4) Å is suggested for the length of the C—OX bond in a primary aliphatic tosylate.

Introduction. We are interested in the effects of substituents on the length of the C—OX bond in series of derivatives of alcohols, ROH. We have demonstrated simple correlations with reactivity in reactions in which this bond is broken ionically (Jones & Kirby, 1979, 1984; Edwards, Jones & Kirby, 1986), and are extending this investigation to examine the effects of β -substituents, in systems based on the general structure Y—CH₂—CH₂—OX. Of primary interest is the sensitivity of the C—OX bond length to changes in *X*, and how this depends on the substituent, *Y*; this change in C—OX bond length is found from the crystal structures of a series of derivatives of a parent alcohol. In the following series of papers we describe an investigation for compounds with *Y* = F. The variation found in C—OX distance then has to be compared with the

variation in the parent series, which in the general case will have *Y* = H. There are large numbers of crystal structures in the literature for simple derivatives of alcohols, such as ethers and esters, and a compilation of mean bond lengths in such systems is available (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). But for specific systems it is necessary to obtain new data. We describe here the structure of the *p*-toluenesulfonate ester of 2-phenylethanol, a key compound for one of our correlations.



Experimental. The title compound was prepared by a general method for arenesulfonate esters. The alcohol (4 mmol) was added slowly to a stirred solution of the sulfonyl chloride (4.5 mmol) in pyridine (2 ml) at 273 K, and the solution stirred for 4 h more. Water (10 ml) was added, and the organic layer, together with diethyl ether extracts, collected and dried over MgSO₄.

2-Phenylethyl *p*-toluenesulfonate was purified by flash column chromatography from Merck Kieselgel 60 (eluant CH₂Cl₂) and recrystallized from CH₂Cl₂–hexane at 268 K to give the title compound as prisms, m.p. 311–312 K [lit. 308.5–309.6 K (Winstein, Lindegren, Marshall & Ingraham, 1953)]. Crystals were grown by the liquid diffusion technique, from CH₂Cl₂–hexane.

Crystal 0.06 × 0.40 × 0.40 mm; Nicolet R3m μ diffractometer, graphite-monochromated Cu *K* α radiation; cell parameters refined from diffractometer angles for 25 centred reflections (50 < 2 θ < 55°).

Intensity data collected by θ - 2θ scans for 4040 reflections with $5 < 2\theta < 116^\circ$ ($h = 9$ to 9 , $k = 9$ to 9 , $l = 27$ to 0); three standard reflections measured every 100 reflections showed no significant crystal decay; absorption correction based on a laminar model and 256 azimuthal scan data, max. and min. transmission factors 0.840 and 0.486; 3401 unique reflections ($R_{\text{int}} 0.010$) with $F > 4\sigma(F)$ were used in the analysis. Structure solved by direct methods and subsequent Fourier difference syntheses. Blocked-cascade least-squares refinement on F , all non-H atoms assigned anisotropic thermal parameters. H atoms were placed in idealized positions and allowed to ride on the relevant C atom, C—H 0.96 Å; each type of H was assigned a common isotropic thermal parameter. 355 parameters, $R = 0.059$, $wR = 0.084$, $w^{-1} = \sigma^2(F) + 0.00217F_o^2$, $S = 1.608$, $\Delta/\sigma = 0.042$ (mean) and 0.343 (max.), $\Delta\rho$ variations within 0.40 and -0.60 e \AA^{-3} . The structure was solved and refined using program system Siemens *SHELXTL-Plus* (Sheldrick, 1990). Neutral-atom scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic coordinates are given in Table 1 and derived parameters in Table 2.* Plots, showing the two molecules in the asymmetric unit and the atom-numbering scheme, appear as Fig. 1.

In the crystal the ester adopts a folded conformation, presumably in response to packing forces, which brings the two aromatic rings into close proximity. Within each molecule the rings are approximately parallel; the dihedral angles between the ring planes are 8.3 and 6.4° , and the distances *ca* 3.7 and 3.6 Å, for molecules (1) and (2), respectively. These distances are slightly greater than the intermolecular ring distances, which have an average value of 3.58 Å, close to the distance expected for graphitic packing. It is reasonable to suppose that the overall conformations of the two molecules are controlled by these inter-ring interactions.

The central torsion angle O(1)—C(1)—C(2)—C(3) is $71.7(3)^\circ$ in molecule (1) and $68.4(3)^\circ$ in molecule (2) so the conformation in the region of primary interest is *gauche*. The C—OTs bond lengths are $1.459(4)$ and $1.465(4)$ Å. These values compare well with the mean value of $1.465(14)$ Å for all sulfonate esters given by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987), and we use a mean value of

* 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 54751 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0051]

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
S(1)	5510 (1)	3626 (1)	3882 (1)	50 (1)
O(1)	4332 (3)	3520 (3)	3337 (1)	58 (1)
O(2)	5401 (3)	5063 (3)	4231 (1)	69 (1)
O(3)	7298 (3)	3505 (3)	3682 (1)	69 (1)
C(1)	2473 (5)	3821 (4)	3385 (1)	66 (1)
C(2)	1198 (4)	2710 (4)	2936 (1)	64 (1)
C(3)	641 (4)	847 (4)	3022 (1)	50 (1)
C(4)	-536 (4)	217 (4)	3447 (1)	58 (1)
C(5)	-1114 (4)	-1515 (4)	3517 (1)	64 (1)
C(6)	-509 (4)	-2645 (4)	3162 (1)	64 (1)
C(7)	656 (5)	-2052 (4)	2747 (1)	68 (1)
C(8)	1239 (4)	-331 (4)	2671 (1)	60 (1)
C(9)	4360 (4)	1733 (3)	4180 (1)	45 (1)
C(10)	3451 (4)	1801 (4)	4673 (1)	55 (1)
C(11)	2507 (4)	266 (4)	4882 (1)	61 (1)
C(12)	2491 (4)	-1295 (4)	4612 (1)	57 (1)
C(13)	3438 (4)	-1313 (4)	4127 (1)	60 (1)
C(14)	4391 (4)	208 (3)	3901 (1)	53 (1)
C(15)	1411 (6)	-2959 (5)	4833 (2)	85 (2)
S(2)	10549 (1)	4161 (1)	1147 (1)	53 (1)
O(4)	9376 (3)	4317 (2)	1675 (1)	56 (1)
O(5)	10420 (3)	5430 (3)	792 (1)	70 (1)
O(6)	12334 (3)	4142 (3)	1363 (1)	77 (1)
C(16)	7522 (4)	4624 (4)	1610 (1)	60 (1)
C(17)	6228 (4)	3695 (4)	2041 (1)	59 (1)
C(18)	5738 (4)	1788 (3)	1951 (1)	48 (1)
C(19)	4620 (4)	914 (4)	1504 (1)	53 (1)
C(20)	4126 (4)	-840 (4)	1429 (1)	60 (1)
C(21)	4788 (4)	-1783 (4)	1801 (1)	63 (1)
C(22)	5896 (4)	-943 (4)	2239 (1)	62 (1)
C(23)	6367 (4)	819 (4)	2315 (1)	58 (1)
C(24)	9424 (4)	2142 (3)	835 (1)	46 (1)
C(25)	8453 (4)	1955 (4)	343 (1)	56 (1)
C(26)	7523 (4)	321 (4)	126 (1)	60 (1)
C(27)	7581 (4)	-1114 (4)	383 (1)	55 (1)
C(28)	8608 (4)	-883 (3)	872 (1)	58 (1)
C(29)	9522 (4)	716 (3)	1103 (1)	53 (1)
C(30)	6537 (5)	-2871 (4)	153 (2)	84 (2)

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

Table 2. Selected bond lengths (Å) and angles ($^\circ$)

S(1)—O(1)	1.569 (2)	S(2)—O(4)	1.562 (2)
S(1)—O(2)	1.411 (2)	S(2)—O(5)	1.418 (2)
S(1)—O(3)	1.429 (2)	S(2)—O(6)	1.423 (2)
S(1)—C(9)	1.757 (3)	S(2)—C(24)	1.744 (2)
O(1)—C(1)	1.459 (4)	O(4)—C(16)	1.465 (4)
C(1)—C(2)	1.514 (4)	C(16)—C(17)	1.520 (4)
C(2)—C(3)	1.492 (4)	C(17)—C(18)	1.494 (4)
O(1)—S(1)—O(2)	110.1 (1)	O(4)—S(2)—O(5)	109.6 (1)
O(1)—S(1)—O(3)	103.0 (1)	O(4)—S(2)—O(6)	103.4 (1)
O(2)—S(1)—O(3)	119.5 (1)	O(5)—S(2)—O(6)	119.8 (1)
O(1)—S(1)—C(9)	103.0 (1)	O(4)—S(2)—C(24)	103.7 (1)
O(2)—S(1)—C(9)	110.2 (1)	O(5)—S(2)—C(24)	109.4 (1)
O(3)—S(1)—C(9)	109.7 (1)	O(6)—S(2)—C(24)	109.5 (1)
S(1)—O(1)—C(1)	117.9 (2)	S(2)—O(4)—C(16)	118.3 (2)
O(1)—C(1)—C(2)	108.6 (3)	O(4)—C(16)—C(17)	108.3 (3)
C(1)—C(2)—C(3)	114.4 (3)	C(16)—C(17)—C(18)	114.2 (3)
C(2)—C(3)—C(4)	121.1 (3)	C(17)—C(18)—C(19)	121.5 (3)
C(2)—C(3)—C(8)	121.4 (3)	C(17)—C(18)—C(23)	121.1 (2)
S(1)—C(9)—C(10)	120.4 (2)	S(2)—C(24)—C(25)	121.4 (2)
S(2)—C(9)—C(14)	117.6 (2)	S(2)—C(24)—C(29)	118.0 (2)

$1.462(4)$ Å in subsequent comparisons involving primary arenesulfonate esters. The mean RCH_2 —OX bond lengths now available, from Allen & Kirby (1984) for aliphatic ethers, aryl alkyl ethers and

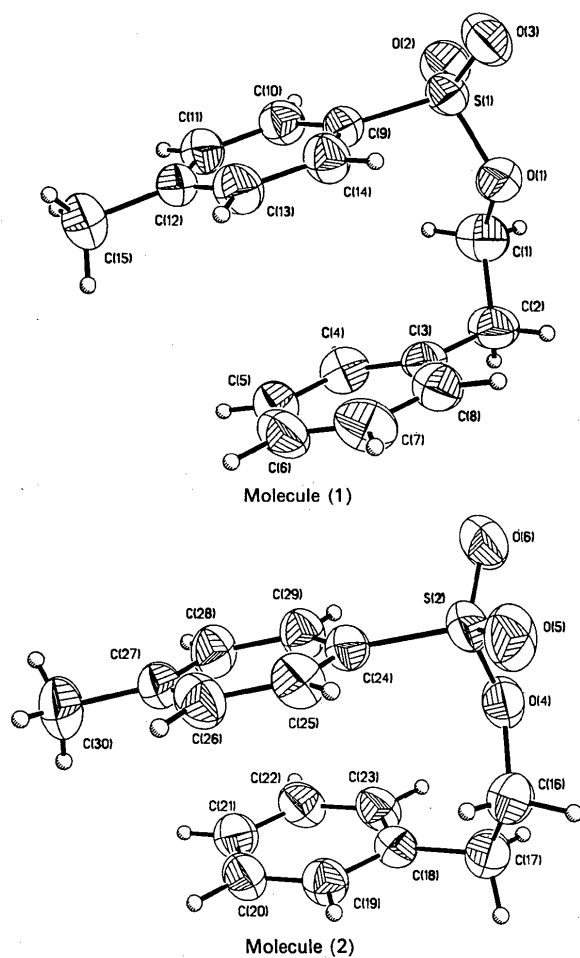


Fig. 1. Molecular structures of the two independent molecules showing the atomic labelling. The thermal ellipsoids are set at the 50% probability level.

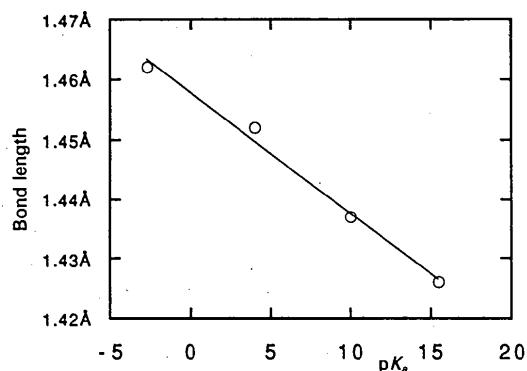


Fig. 2. Plot of bond length for various $R-OX$ (see text) vs the pK_a of the conjugate acid, HOX , of the leaving group. The correlation coefficient of the least-squares fit is 0.995.

esters, and from this work for tosylates, give the expected (Jones & Kirby, 1984) good linear relationship with the pK_a (of the conjugate acid) of the leaving group, XO^- , over a range of 10^{18} in dissociation constant (Fig. 2).

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