

Bond Length and Reactivity: 1-Arylethyl Ethers and Esters. 6.* Structure of 1-(4-Nitrophenyl)ethyl 2-Naphthalenesulfonate

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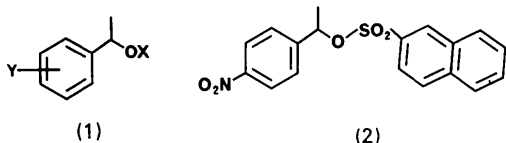
(Received 14 November 1985; accepted 21 April 1986)

Abstract. $C_{18}H_{15}NO_5S$, $M_r = 357.28$, monoclinic, $P2_1/n$, $a = 7.286$ (1), $b = 30.012$ (5), $c = 7.814$ (2) Å, $\beta = 103.63$ (2)°, $U = 1660.6$ Å³, $Z = 4$, $D_x = 1.43$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.2$ mm⁻¹, $F(000) = 744$, $T = 293$ K, $R = 0.053$ for 2745 reflections. The title compound crystallizes in a folded conformation with the ring systems of the molecule almost parallel. The C–O bond at the benzylic centre is at 1.476 (3) Å the longest yet found in the series of 1-(4-nitrophenyl)ethanol derivatives.

Introduction. As part of our wider investigation of correlations between the length of a bond in the crystal and the rate at which it is broken in solution (Jones & Kirby, 1984) we have reported crystal structures for a series of derivatives (1) of 1-arylethanol (Jones, Edwards & Kirby, 1986*a,b,c,d*; Jones, Sheldrick, Edwards & Kirby, 1986).

Of ten compounds studied so far, none has the best, and therefore potentially the most interesting, arene sulfonate leaving group ($X = \text{SO}_2\text{Ar}$). With electron-donating substituents Y such compounds are not stable enough: in other cases suitable crystals could not be obtained. We were able to make, crystallize and solve the structure of the stable *p*-toluenesulfonate of the 4-nitro compound (1), $Y = 4\text{-NO}_2$, $X = \text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$ -*p*, but a minor disorder component affected apparent interatomic distances in the region of most interest, and these data could not be used.

Here we report data for a similar compound, the 2-naphthalenesulfonate (2), which did give a satisfactory structure.



* Part 5: Jones, Edwards & Kirby (1986*d*).

Experimental. The sulfonate ester (2) was prepared by the reaction of the parent alcohol with 2-naphthalenesulfonyl chloride in methylene chloride, using 4-dimethylaminopyridine as the base. Colourless prisms, m.p. 374–375 K (dec.), were grown by diffusing hexane into a solution in methylene chloride.

Stoe–Siemens four-circle diffractometer, monochromated Mo $K\alpha$ radiation, profile-fitting mode (Clegg, 1981). 4430 intensities ($2\theta_{\text{max}} 55^\circ$, $-h+k\pm l$ and some $+h$ equivalents). Three check reflections, no systematic intensity variation. Crystal size $0.7 \times 0.6 \times 0.3$ mm; no absorption correction. 3906 unique reflections ($R_{\text{int}} 0.022$), 2745 with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*; Sheldrick, 1978). Index range $|h| \leq 9$, $|k| \leq 38$, $|l| \leq 10$. Cell constants refined from $\pm 2\theta$ values of 54 reflections in the range $20\text{--}23^\circ$. Structure solution by routine direct methods. Refinement on F to $R 0.053$, $wR 0.056$ [all non-H atoms anisotropic; H included using riding model with C–H 0.96 Å, H–C–H 109.5° , $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$]; weighting scheme $w^{-1} = \sigma^2(F) + 0.0002F^2$; 229 parameters; $S 2.1$; max. $\Delta/\sigma 0.007$; max. and min. features in final $\Delta\rho$ synthesis $+0.2$, -0.4 e Å⁻³. Atomic scattering factors as incorporated in *SHELXTL*.†

Discussion. Final atom coordinates are presented in Tables 1 and 2, and a thermal-ellipsoid plot of (2), showing the atom-numbering scheme, appears in Fig. 1.

Like another 2-naphthalenesulfonate (of 4-phenylcyclohexanone oxime; Jones, Edwards & Kirby, 1986*e*) we have reported recently, (2) crystallizes in a folded conformation, with the naphthalene system above, and inclined at only 12° to, the 4-nitrophenyl

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43010 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

ring. The distance between these aromatic systems is *ca* 3.4 Å, somewhat less than the intermolecular distance between naphthalene residues (*ca* 3.6 Å at 2-*x*, -*y*, 1-*z*), which are however not perfectly stacked (only the outer rings overlap; see Fig. 2).

Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{Å}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U*</i>
S	9587 (1)	1718.4 (2)	8093 (1)	69 (1)
O(1)	7654 (2)	1938.8 (5)	8186 (2)	58 (1)
O(2)	10483 (2)	1991 (1)	7027 (3)	99 (1)
O(3)	10461 (3)	1636 (1)	9884 (3)	118 (1)
C(3)	6538 (3)	2202 (1)	6709 (3)	52 (1)
C(4)	5126 (4)	2445 (1)	7471 (3)	64 (1)
C(21)	5705 (3)	1904 (1)	5175 (3)	43 (1)
C(22)	4562 (3)	1542 (1)	5348 (3)	49 (1)
C(23)	3914 (3)	1256 (1)	3966 (3)	47 (1)
C(24)	4395 (3)	1335 (1)	2393 (2)	43 (1)
C(25)	5466 (3)	1694 (1)	2149 (3)	52 (1)
C(26)	6117 (3)	1978 (1)	3565 (3)	50 (1)
N	3793 (3)	1016 (1)	933 (2)	57 (1)
O(41)	2916 (3)	685 (1)	1204 (2)	87 (1)
O(42)	4209 (3)	1093 (1)	-451 (2)	85 (1)
C(11)	9238 (3)	1143 (1)	5374 (3)	46 (1)
C(12)	8959 (3)	1211 (1)	7015 (3)	48 (1)
C(13)	8095 (3)	884 (1)	7857 (3)	56 (1)
C(14)	7554 (3)	494 (1)	7039 (3)	55 (1)
C(14a)	7813 (3)	409 (1)	5331 (3)	45 (1)
C(15)	7263 (3)	4 (1)	4448 (3)	61 (1)
C(16)	7536 (4)	-70 (1)	2808 (3)	71 (1)
C(17)	8378 (4)	258 (1)	1976 (3)	69 (1)
C(18)	8922 (3)	650 (1)	2774 (3)	57 (1)
C(18a)	8669 (3)	740 (1)	4481 (3)	43 (1)

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

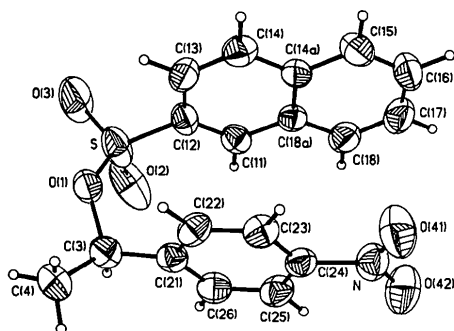


Fig. 1. Thermal-ellipsoid plot of (2), showing the atom-numbering scheme.

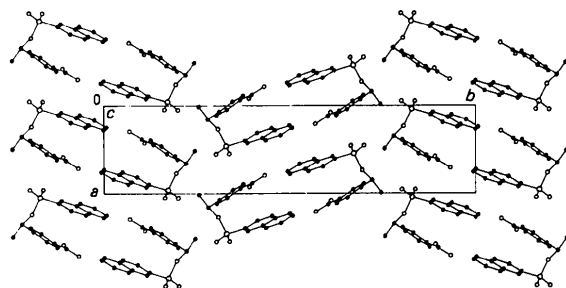


Fig. 2. Packing plot of (2) projected down *c*.

This conformational preference is reflected in a conformation about C(3)—C(21) unusual for this series, the two bonds C(3)—C(4) and C(3)—O(1) being almost equally staggered with respect to the aromatic ring [dihedral angles -61.9 (4), 56.2 (4) $^\circ$], so that the benzylic H atom must be eclipsing it.

The length of the bond C(3)—O(1), 1.476 (3) Å, at the benzylic centre is, as expected, the longest found in the four derivatives of (4-nitrophenyl)ethanol that we have now reported; we have previously measured values of 1.433, 1.452 and 1.466 Å for the triphenylmethyl ether, the chloroacetate ester and the diphenyl phosphate ester (Jones, Sheldrick, Edwards & Kirby, 1986; Jones, Edwards & Kirby, 1986*b,d*). There is some uncertainty about the pK_a 's of diphenyl

Table 2. Bond lengths (Å), bond angles and torsion angles ($^\circ$)

O(1)—S	1.573 (3)	O(2)—S	1.430 (3)
O(3)—S	1.416 (3)	C(3)—O(1)	1.476 (3)
C(3)—C(4)	1.494 (5)	C(21)—C(3)	1.506 (4)
C(21)—C(22)	1.395 (4)	C(21)—C(26)	1.379 (4)
C(22)—C(23)	1.373 (4)	C(23)—C(24)	1.376 (4)
C(24)—C(25)	1.371 (4)	C(24)—N	1.475 (4)
C(25)—C(26)	1.389 (4)	N—O(41)	1.225 (4)
N—O(42)	1.212 (4)	C(11)—C(12)	1.361 (4)
C(11)—C(18a)	1.411 (4)	C(12)—S	1.748 (3)
C(12)—C(13)	1.409 (4)	C(13)—C(14)	1.348 (4)
C(14)—C(14a)	1.414 (4)	C(14a)—C(15)	1.410 (4)
C(14a)—C(18a)	1.417 (4)	C(15)—C(16)	1.360 (5)
C(16)—C(17)	1.399 (5)	C(17)—C(18)	1.347 (4)
C(18)—C(18a)	1.414 (4)		
O(1)—S—O(2)	108.8 (2)	O(1)—S—O(3)	103.1 (2)
O(2)—S—O(3)	121.0 (2)	O(1)—S—C(12)	104.6 (2)
O(2)—S—C(12)	108.8 (2)	O(3)—S—C(12)	109.2 (2)
S—O(1)—C(3)	121.6 (2)	O(1)—C(3)—C(4)	104.7 (3)
O(1)—C(3)—C(21)	110.4 (3)	C(4)—C(3)—C(21)	114.9 (3)
C(3)—C(21)—C(22)	121.6 (3)	C(3)—C(21)—C(26)	119.8 (3)
C(22)—C(21)—C(26)	118.6 (3)	C(21)—C(22)—C(23)	120.9 (3)
C(22)—C(23)—C(24)	118.8 (3)	C(23)—C(24)—C(25)	122.2 (3)
C(23)—C(24)—N	119.2 (3)	C(25)—C(24)—N	118.6 (3)
C(24)—C(25)—C(26)	118.1 (3)	C(21)—C(26)—C(25)	121.3 (3)
C(24)—N—O(41)	117.6 (3)	C(24)—N—O(42)	118.4 (3)
O(41)—N—O(42)	124.0 (3)	C(12)—C(11)—C(18a)	120.1 (3)
S—C(12)—C(11)	120.2 (3)	S—C(12)—C(13)	118.5 (3)
C(11)—C(12)—C(13)	121.3 (3)	C(12)—C(13)—C(14)	119.7 (3)
C(13)—C(14)—C(14a)	121.0 (3)	C(14)—C(14a)—C(15)	122.1 (3)
C(14)—C(14a)—C(18a)	119.1 (3)	C(15)—C(14a)—C(18a)	118.7 (3)
C(14a)—C(15)—C(16)	120.9 (3)	C(15)—C(16)—C(17)	120.1 (3)
C(16)—C(17)—C(18)	120.9 (3)	C(17)—C(18)—C(18a)	120.9 (3)
C(11)—C(18a)—C(14a)	118.7 (3)	C(11)—C(18a)—C(18)	122.7 (3)
C(14a)—C(18a)—C(18)	118.6 (3)		

O(2)—S—O(1)—C(3)	31.4 (3)	O(3)—S—O(1)—C(3)	161.0 (3)
C(12)—S—O(1)—C(3)	-84.7 (3)	O(1)—S—C(12)—C(11)	112.1 (3)
O(1)—S—C(12)—C(13)	-65.5 (3)	O(2)—S—C(12)—C(11)	-4.1 (3)
O(2)—S—C(12)—C(13)	178.3 (3)	O(3)—S—C(12)—C(11)	-138.2 (3)
O(3)—S—C(12)—C(13)	44.3 (3)	S—O(1)—C(3)—C(4)	-165.7 (2)
S—O(1)—C(3)—C(21)	70.1 (3)	O(1)—C(3)—C(21)—C(22)	56.2 (4)
O(1)—C(3)—C(21)—C(26)	-121.9 (3)	C(4)—C(3)—C(21)—C(22)	-61.9 (4)
C(4)—C(3)—C(21)—C(26)	120.0 (3)	C(23)—C(24)—N—O(42)	179.1 (3)
C(23)—C(24)—N—O(41)	-1.6 (4)	C(25)—C(24)—N—O(42)	-2.7 (4)
C(25)—C(24)—N—O(41)	176.6 (3)		

Sign convention as defined by Klyne & Prelog (1960).

phosphoric and 2-naphthalenesulfonic acids, and the comparison involves three good leaving groups with one (Ph_3CO^-) very poor one; but the bond length – $\text{p}K_a$ plot (Jones & Kirby, 1979, 1984) is not a very good straight line (correlation coefficient r 0.935). Nevertheless it is clear that (i) other things being equal, the bond to the better-leaving-group O atom is longer, and (ii) that electron withdrawal in the aromatic ring reduces the effect, as shown by the decrease in the length of the C(3)–O(1) bond from 1.481 to 1.452 Å when the 4-nitro group is introduced into the esters (Jones, Edwards & Kirby, 1986a,b).

The structures of all the compounds in this series will be discussed in more detail, in the context of the C–O cleavage reaction, in a forthcoming paper (Edwards, Jones & Kirby, 1986).

PGJ thanks the Verband der Chemischen Industrie and the Cambridge Philosophical Society for financial support.

Acta Cryst. (1986). C42, 1372–1374

Bond Length and Reactivity. Structure of a Grob Fragmentation Substrate, 4 α ,5 β ,8 $\alpha\beta$ -1-Methyldecahydroquinolin-5-yl 3,5-Dinitrobenzoate

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(Received 14 November 1985; accepted 21 April 1986)

Abstract. $\text{C}_{17}\text{H}_{21}\text{N}_3\text{O}_6$, $M_r = 363.38$, orthorhombic, $Pbca$, $a = 6.338$ (2), $b = 25.355$ (8), $c = 21.774$ (6) Å, $U = 3499$ Å³, $Z = 8$, $D_x = 1.38$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.1$ mm⁻¹, $F(000) = 1536$, $T = 293$ K, $R = 0.089$ for 1758 reflections. The compound crystallizes in the chair,chair conformation with *O*-acyl and *N*-methyl substituents equatorial. The C–O-acyl bond [1.470 (5) Å] is relatively long because of the usual $\text{C}^+ - \text{O}^-$ contribution in this type of compound. There is no evidence for involvement of the σ electrons of the C(4 α)–C(8 α) bond in an exceptional $\sigma - \sigma_{\text{C}-\text{O}}^*$ interaction.

Introduction. As part of an extensive investigation of the relationship between the length of a bond in the crystal and the rate at which it is broken in ionic

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reaction in solution (Jones & Kirby, 1984), we reported crystal structures for a set of equatorial tetrahydropyranyl acetals (aryloxytetrahydropyrans), such as (1) (Jones & Kirby, 1982; Briggs, Glenn, Jones, Kirby & Ramaswamy, 1984). These showed a remarkable trend in the pattern of bond lengths at the acetal centre: as the fragment ArO^- is made a better leaving group, by the addition of electron-withdrawing substituents, the usual (Briggs *et al.*, 1984) lengthening of the C–OAr bond and concomitant shortening of O–COAr is accompanied by a significant extension of the remote $\text{C}^* - \text{O}$ bond. We interpreted this as evidence for an incipient fragmentation reaction (1→2), valence tautomer (2) making an increasingly important contribution to the structure of the ground state as the anion ArO^- becomes more stable.