

Bond Length and Reactivity: 1-Arylethyl Ethers and Esters. 4.* Structures of Two *p*-Nitrophenyl Ethers of 1-Arylethanol. 1-Phenylethyl and 1-(4-Methoxy)phenylethyl 4-Nitrophenyl Ethers

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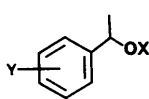
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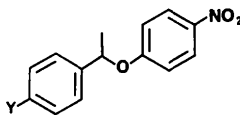
(Received 14 November 1985; accepted 21 April 1986)

Abstract. $C_{14}H_{13}NO_3$ (2a), $M_r = 243.27$, triclinic, $P\bar{1}$, $a = 10.268$ (4), $b = 11.115$ (5), $c = 12.303$ (5) Å, $\alpha = 112.15$ (3), $\beta = 91.94$ (3), $\gamma = 100.18$ (3)°, $U = 1272.2$ Å³, $Z = 4$, $D_x = 1.27$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.08$ mm⁻¹, $F(000) = 512$, $T = 293$ K, $R = 0.060$ for 2480 reflections. $C_{15}H_{15}NO_4$ (2b), $M_r = 273.29$, monoclinic, $P2_1/n$, $a = 6.548$ (1), $b = 7.898$ (1), $c = 26.947$ (5) Å, $\beta = 94.35$ (2)°, $U = 1389.5$ Å³, $Z = 4$, $D_x = 1.31$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.09$ mm⁻¹, $F(000) = 576$, $T = 293$ K, $R = 0.052$ for 1699 reflections. The C–O bond length at the benzylic centre is 1.448 (4) Å in (2b) and 1.450 (4) Å in one independent molecule of (2a), but appreciably shorter [1.420 (5) Å] in the other molecule of (2a). This difference may be attributed, at least in part, to the reduced electronegativity of the O atom, in turn caused by the rotation of the NO₂ group out of the aromatic ring plane.

Introduction. As part of our broader investigations of bond length and reactivity (Jones & Kirby, 1984), we are looking at structures of a series of derivatives (1) of 1-arylethanol, where we can vary systematically both *X* and *Y*. So far we have reported results for four aryl-substituted esters (Jones, Edwards & Kirby, 1986*a,b*) and three triphenylmethyl ethers (Jones, Sheldrick, Edwards & Kirby, 1986). In this paper we report the structures of two 4-nitrophenyl ethers, (2a) and (2b). We have not yet been able to produce suitable crystals of other compounds in this series.



(1)

(2a) Y = H
(2b) Y = OCH₃

Experimental. The parent alcohols were arylated, after conversion to the alkoxides with NaH, using *p*-fluoronitrobenzene in tetrahydrofuran, in the presence of tetrabutylammonium fluoride. Crystals were grown by diffusing pentane into a solution in diisopropyl ether [(2a), pale yellow, irregular, m.p. 339–341 K] or petrol into an ether solution [(2b), colourless tablets, m.p. 335–336 K].

{Values for (2b), where differing from (2a), are given in braces.} Stoe–Siemens four-circle diffractometer, monochromated Mo *K*α radiation; profile-fitting mode (Clegg, 1981). Crystal 0.65 × 0.45 × 0.2 {0.6 × 0.66 × 0.25} mm; 2θ_{max} 50°, $-h+k+l$ { $+h+k+l$ }; 4679 {2674} intensities recorded. Three check reflections, no systematic intensity change. No absorption correction. R_{int} 0.020 {0.015} for 4466 {2446} unique reflections, of which 2480 {1699} with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*; Sheldrick, 1978). Index ranges after merging: $|h| \leq 12$ {7}, $|k| \leq 13$ {9}, $|l| \leq 14$ {31}. Cell constants refined from $\pm 2\theta$ values of 31 {38} reflections in the range 20–23°. Structure solution by routine direct methods. Refinement on F to R 0.060 {0.052}, wR 0.059 {0.055}. All non-H atoms anisotropic; H atoms included using riding model [C–H 0.96 Å, H–C–H 109.5°, $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$]. Weighting scheme $w^{-1} = \sigma^2(F) + gF^2$ with g 0.0003 {0.00025}. 331 {187} parameters. $S = 1.85$ {1.96}; max. Δ/σ 0.06 {0.05}; max. and min. features in final $\Delta\rho$ map +0.24, –0.23 {+0.16, –0.22} e Å⁻³. Atomic scattering factors as incorporated in *SHELXTL*.†

† 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 43008 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Part 3: Jones, Sheldrick, Edwards & Kirby (1986).

Discussion. Final atom coordinates and derived parameters are presented in Tables 1–4, thermal-ellipsoid plots in Figs. 1 and 2. The two independent molecules of (2a) are compared in Fig. 3.

The two independent molecules of (2a), and that of (2b), crystallize in broadly similar conformations. The 4-nitrophenyl ether system is close to planar, as is the 4-methoxybenzyl system of (2b), and the dihedral angle C(4)–C(3)–C(21)–C(22 or 26) lies between 100 and 104.8° for the three molecules.

Unexpectedly, the differences in bond lengths and angles between (2a) and (2b) are smaller than those between the two independent molecules of (2a). In particular, the bond length C(3)–O(1), which is 1.448 (4) Å in (2b) and 1.450 (4) Å in molecule 1 of (2a), is very short, 1.420 (5) Å, in molecule 2. This result is disturbing, because our use of bond length as an index of reactivity depends on accurate measurement of interatomic distances, and attributes significance to small differences between related structures. The difference in the present case seems to be real, rather than a result of systematic error, to the extent that, of the three bonds at the C(3) centre involved, one is shorter, one is longer, and one has the

same length in molecule 1 compared with molecule 2. It is therefore important to identify the origin of the apparent discrepancy.

Table 2. Bond lengths (Å), bond angles and torsion angles (°) for (2a)

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
C(3)–O(1)	1.450 (4)	1.420 (5)	C(3)–O(1)–C(11)	119.2 (3)	120.6 (4)	C(11)–O(1)	1.357 (4)
C(11)–O(1)	1.357 (4)	1.373 (5)	O(1)–C(3)–C(21)	111.0 (3)	110.7 (3)	C(11)–C(16)	1.392 (5)
C(11)–C(16)	1.392 (5)	1.376 (5)	O(1)–C(11)–C(12)	124.6 (3)	124.6 (3)	C(13)–C(14)	1.368 (5)
C(13)–C(14)	1.368 (5)	1.364 (5)	C(12)–C(11)–C(16)	120.3 (3)	120.5 (4)	C(14)–N(4)	1.455 (4)
C(14)–N(4)	1.455 (4)	1.456 (5)	C(12)–C(13)–C(14)	120.5 (4)	119.3 (4)	N(4)–O(41)	1.221 (5)
N(4)–O(41)	1.221 (5)	1.218 (5)	C(13)–C(14)–N(4)	119.8 (4)	119.5 (4)	C(21)–C(3)	1.512 (6)
C(21)–C(3)	1.512 (6)	1.511 (6)	C(14)–C(15)–C(16)	119.5 (4)	118.9 (3)	C(21)–C(26)	1.383 (5)
C(21)–C(26)	1.383 (5)	1.361 (6)	C(14)–N(4)–O(41)	118.7 (3)	118.2 (3)	C(23)–C(24)	1.371 (6)
C(23)–C(24)	1.371 (6)	1.355 (8)	O(41)–N(4)–O(42)	123.4 (3)	123.4 (4)	C(25)–C(26)	1.384 (7)
C(25)–C(26)	1.384 (7)	1.375 (7)	C(3)–C(21)–C(26)	120.6 (4)	120.1 (4)	C(3)–C(4)	1.507 (5)
C(3)–C(4)	1.507 (5)	1.517 (7)	C(21)–C(22)–C(23)	121.0 (4)	120.0 (5)	C(11)–C(12)	1.380 (5)
C(11)–C(12)	1.380 (5)	1.372 (5)	C(23)–C(24)–C(25)	120.1 (5)	120.1 (5)	C(12)–C(13)	1.373 (4)
C(12)–C(13)	1.373 (4)	1.379 (6)	C(21)–C(26)–C(25)	120.2 (4)	120.8 (4)	C(14)–C(15)	1.370 (5)
C(14)–C(15)	1.370 (5)	1.374 (5)	O(1)–C(3)–C(4)	105.9 (3)	107.7 (4)	C(15)–C(16)	1.371 (4)
C(15)–C(16)	1.371 (4)	1.357 (6)	C(4)–C(3)–C(21)	111.4 (4)	112.2 (4)	N(4)–O(42)	1.224 (4)
N(4)–O(42)	1.224 (4)	1.214 (4)	O(1)–C(11)–C(16)	115.1 (3)	114.9 (4)	C(21)–C(22)	1.377 (6)
C(21)–C(22)	1.377 (6)	1.373 (5)	C(11)–C(12)–C(13)	119.0 (3)	119.2 (3)	C(22)–C(23)	1.376 (6)
C(22)–C(23)	1.376 (6)	1.393 (7)	C(13)–C(14)–C(15)	120.9 (3)	121.6 (4)	C(24)–C(25)	1.367 (7)
C(24)–C(25)	1.367 (7)	1.348 (6)	C(15)–C(14)–N(4)	119.3 (3)	118.9 (3)		
			C(11)–C(16)–C(15)	119.8 (4)	120.5 (4)		
			C(14)–N(4)–O(42)	117.9 (3)	118.5 (4)		
			C(3)–C(21)–C(22)	120.7 (4)	121.1 (4)		
			C(22)–C(21)–C(26)	118.7 (4)	118.8 (5)		
			C(22)–C(23)–C(24)	119.8 (4)	119.9 (4)		
			C(24)–C(25)–C(26)	120.2 (4)	120.4 (5)		

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

Atoms of the second molecule are distinguished by primes (').

	x	y	z	U*
O(1)	379 (2)	3803 (2)	873 (2)	76 (1)
C(3)	779 (3)	2705 (3)	–45 (2)	72 (1)
C(4)	–455 (3)	1626 (3)	–522 (3)	94 (2)
C(11)	1225 (2)	5003 (2)	1327 (2)	64 (1)
C(12)	2363 (3)	5340 (2)	851 (2)	71 (1)
C(13)	3136 (3)	6592 (3)	1395 (3)	71 (1)
C(14)	2791 (3)	7488 (2)	2399 (2)	68 (1)
C(15)	1659 (3)	7166 (3)	2874 (3)	80 (1)
C(16)	867 (3)	5926 (3)	2339 (3)	79 (1)
N(4)	3629 (2)	8806 (2)	2970 (2)	87 (1)
O(41)	4661 (2)	9065 (2)	2565 (2)	111 (1)
O(42)	3265 (2)	9595 (2)	3845 (2)	127 (1)
C(21)	1874 (3)	2241 (2)	442 (2)	61 (1)
C(22)	1786 (3)	2046 (3)	1480 (3)	73 (1)
C(23)	2731 (3)	1531 (3)	1885 (3)	83 (1)
C(24)	3779 (3)	1208 (3)	1250 (3)	90 (2)
C(25)	3897 (3)	1416 (3)	229 (3)	93 (2)
C(26)	2949 (3)	1934 (3)	–179 (3)	78 (1)
O(1')	3007 (2)	6249 (2)	5919 (2)	100 (1)
C(3')	2774 (3)	7422 (3)	6815 (3)	91 (2)
C(4')	2483 (4)	7114 (4)	7894 (3)	123 (2)
C(11')	3798 (3)	6320 (3)	5059 (3)	70 (1)
C(12')	4694 (3)	7432 (3)	5139 (3)	73 (1)
C(13')	5514 (3)	7350 (3)	4260 (3)	72 (1)
C(14')	5392 (3)	6175 (3)	3314 (2)	67 (1)
C(15')	4462 (3)	5074 (3)	3209 (3)	79 (1)
C(16')	3680 (3)	5150 (3)	4090 (3)	81 (1)
N(4')	6237 (3)	6092 (3)	2372 (2)	99 (1)
O(41')	7203 (3)	6984 (3)	2561 (3)	142 (2)
O(42')	5943 (3)	5141 (3)	1440 (2)	138 (2)
C(21')	1648 (3)	7901 (3)	6387 (3)	75 (1)
C(22')	503 (3)	7030 (4)	5763 (3)	103 (2)
C(23')	–547 (3)	7505 (4)	5433 (3)	124 (2)
C(24')	–442 (4)	8827 (4)	5740 (3)	131 (2)
C(25')	685 (4)	6851 (4)	6345 (4)	126 (2)
C(26')	1732 (4)	9222 (3)	6667 (3)	99 (2)

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

	Molecule 1	Molecule 2
C(11)–O(1)–C(3)–C(21)	70.2 (4)	84.0 (4)
C(3)–O(1)–C(11)–C(16)	–169.0 (4)	–164.3 (4)
O(1)–C(3)–C(21)–C(26)	–137.4 (3)	–139.7 (4)
C(4)–C(3)–C(21)–C(26)	104.8 (4)	100.0 (5)
C(13)–C(14)–N(4)–O(41)	–3.2 (6)	14.6 (6)
C(15)–C(14)–N(4)–O(41)	177.2 (4)	–167.3 (5)
C(11)–O(1)–C(3)–C(4)	–168.7 (4)	–153.1 (4)
C(3)–O(1)–C(11)–C(12)	11.6 (6)	18.6 (6)
O(1)–C(3)–C(21)–C(22)	46.2 (4)	43.5 (5)
C(4)–C(3)–C(21)–C(22)	–71.6 (4)	–76.9 (5)
O(1)–C(11)–C(12)–C(13)	179.9 (4)	174.5 (4)
O(1)–C(11)–C(16)–C(15)	179.5 (4)	–176.4 (4)
C(13)–C(14)–N(4)–O(42)	177.6 (4)	–165.4 (4)
C(15)–C(14)–N(4)–O(42)	–2.0 (6)	12.7 (6)

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

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

	x	y	z	U*
O(1)	8015 (2)	3087 (2)	1043 (1)	62 (1)
C(3)	7496 (3)	1372 (3)	1176 (1)	59 (1)
C(4)	9500 (4)	417 (4)	1194 (1)	80 (1)
C(11)	6509 (3)	4169 (3)	869 (1)	50 (1)
C(12)	7143 (4)	5817 (3)	805 (1)	62 (1)
C(13)	5826 (4)	7010 (3)	604 (1)	64 (1)
C(14)	3823 (4)	6553 (3)	474 (1)	54 (1)
C(15)	3143 (3)	4928 (3)	534 (1)	54 (1)
C(16)	4488 (3)	3718 (3)	736 (1)	54 (1)
N(4)	2417 (4)	7828 (3)	253 (1)	73 (1)
O(41)	675 (3)	7399 (3)	115 (1)	95 (1)
O(42)	3033 (3)	9279 (3)	221 (1)	117 (1)
C(21)	6507 (3)	1363 (3)	1665 (1)	50 (1)
C(22)	4862 (3)	349 (3)	1739 (1)	55 (1)
C(23)	3969 (3)	308 (3)	2190 (1)	57 (1)
C(24)	4750 (3)	1329 (3)	2575 (1)	57 (1)
C(25)	6413 (4)	2338 (3)	2506 (1)	68 (1)
C(26)	7284 (4)	2361 (3)	2060 (1)	66 (1)
O(24)	3968 (3)	1427 (2)	3032 (1)	78 (1)
C(27)	2150 (4)	506 (4)	3104 (1)	94 (1)

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

The largest difference between molecules 1 and 2 of (2a) is in the angle between the planes defined by the nitrophenoxy ring and the 4-nitro group. These are close to coplanar in molecule 1 (mean dihedral angle 2.2°), but the nitro group in molecule 2 is rotated out of plane by $13.6 (10)^\circ$. If this rotation were sufficient to reduce π, π overlap between the nitro group and the ring, and hence the ether O atom, substantially, the 'effective electronegativity' of this O atom would be reduced. This could explain at least part of the apparent shortening of C(3)—O(1) in molecule 2; the length of this bond in molecule 1 is that expected for a secondary alkyl aryl ether (Allen & Kirby, 1984). (We could find no directly relevant information on this question in the small number of 4-nitrophenoxy compounds in the Cambridge Crystallographic Datafile.) Thus for bond length—reactivity correlations we will use, with obvious reservations, the data for molecule 1. For structure—structure correlations both molecules are equally useful.

It is also of particular interest for the present investigation that the introduction of the electron-donating 4-methoxy group does not result in a significant shortening of C(3)—O(1). This confirms the result found with the corresponding 3,5-dinitrobenzoate esters (Jones, Edwards & Kirby, 1986a), and will be discussed in the context of all the structural data on these systems (1), in a forthcoming paper (Edwards, Jones & Kirby, 1986).

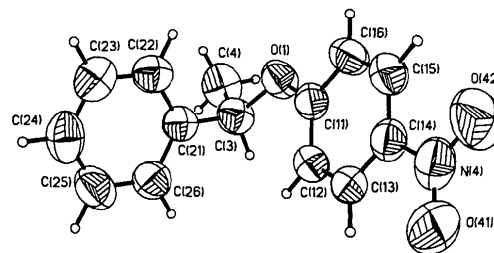


Fig. 1. Thermal-ellipsoid plot of molecule 1 of (2a), showing the atom-numbering scheme.

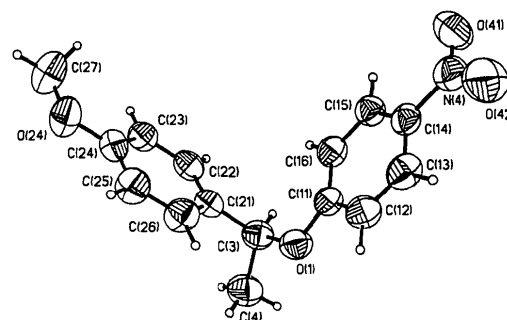


Fig. 2. Thermal-ellipsoid plot of (2b), showing the atom-numbering scheme.

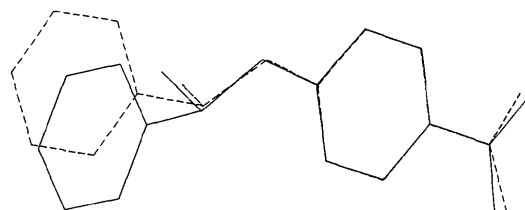


Fig. 3. Least-squares fit of the two independent molecules of (2a) [atoms fitted: C(11)—C(16), molecule 2 dotted].

Table 4. Bond lengths (Å), bond angles and torsion angles ($^\circ$) for (2b)

C(3)—O(1)	1.448 (4)	C(3)—C(4)	1.511 (4)
C(11)—O(1)	1.362 (4)	C(11)—C(12)	1.381 (4)
C(11)—C(16)	1.391 (4)	C(12)—C(13)	1.362 (4)
C(13)—C(14)	1.380 (4)	C(14)—C(15)	1.372 (4)
C(14)—N(4)	1.460 (4)	C(15)—C(16)	1.383 (4)
N(4)—O(41)	1.220 (4)	N(4)—O(42)	1.220 (4)
C(21)—C(3)	1.511 (4)	C(21)—C(22)	1.368 (4)
C(21)—C(26)	1.389 (4)	C(22)—C(23)	1.390 (4)
C(23)—C(24)	1.381 (4)	C(24)—C(25)	1.374 (4)
C(24)—O(24)	1.369 (4)	C(15)—C(26)	1.370 (5)
C(27)—O(24)	1.421 (5)		
C(3)—O(1)—C(11)	119.7 (3)	O(1)—C(3)—C(4)	104.8 (3)
O(1)—C(3)—C(21)	110.1 (3)	C(4)—C(3)—C(21)	113.5 (3)
O(1)—C(11)—C(12)	114.7 (3)	O(1)—C(11)—C(16)	125.3 (3)
C(12)—C(11)—C(16)	119.9 (3)	C(11)—C(12)—C(13)	120.9 (3)
C(12)—C(13)—C(14)	118.7 (3)	C(13)—C(14)—C(15)	121.7 (3)
C(13)—C(14)—N(4)	118.7 (3)	C(15)—C(14)—N(4)	119.5 (3)
C(14)—C(15)—C(16)	119.4 (3)	C(11)—C(16)—C(15)	119.3 (3)
C(14)—N(4)—O(41)	118.6 (3)	C(14)—N(4)—O(42)	118.4 (3)
O(41)—N(4)—O(42)	123.0 (3)	C(3)—C(21)—C(22)	121.5 (3)
C(3)—C(21)—C(26)	120.5 (3)	C(22)—C(21)—C(26)	117.9 (3)
C(21)—C(22)—C(23)	121.9 (3)	C(22)—C(23)—C(24)	119.2 (3)
C(23)—C(24)—C(25)	119.3 (3)	C(23)—C(24)—O(24)	124.4 (3)
C(25)—C(24)—O(24)	116.3 (3)	C(24)—C(25)—C(26)	120.9 (3)
C(21)—C(26)—C(25)	120.8 (3)	C(24)—O(24)—C(27)	117.9 (3)
C(11)—O(1)—C(3)—C(4)	162.8 (3)	C(11)—O(1)—C(3)—C(21)	-74.8 (3)
C(3)—O(1)—C(11)—C(12)	173.3 (3)	C(3)—O(1)—C(11)—C(16)	-9.6 (4)
O(1)—C(3)—C(21)—C(22)	139.1 (3)	O(1)—C(3)—C(21)—C(26)	-42.5 (4)
C(4)—C(3)—C(21)—C(22)	-103.8 (3)	C(4)—C(3)—C(21)—C(26)	74.5 (4)
C(13)—C(14)—N(4)—O(41)	176.3 (3)	C(13)—C(14)—N(4)—O(42)	-4.7 (5)
C(15)—C(14)—N(4)—O(41)	-1.9 (4)	C(15)—C(14)—N(4)—O(42)	177.2 (3)
C(23)—C(24)—O(24)—C(27)	-4.4 (4)	C(25)—C(24)—O(24)—C(27)	175.1 (3)

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

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

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