

Bond Length and Reactivity. The Effect of β -Fluorine. Structures of the 4-Nitrophenyl Ether and the 4-Nitrobenzoate Ester of 2-Fluoro-2-phenylethanol

BY PETER G. JONES

*Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30,
3300 Braunschweig, Germany*

ANGELIKA DÖLLE

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, Germany

AND ANTHONY J. KIRBY AND JANE K. PARKER

University Chemical Laboratory, Cambridge CB2 1EW, England

(Received 14 January 1991; accepted 14 October 1991)

Abstract. 2-Fluoro-2-phenylethyl 4-nitrophenyl ether, (1), $C_{14}H_{12}FNO_3$, $M_r = 261.25$, monoclinic, $P2_1/n$, $a = 8.3330$ (16), $b = 5.5554$ (16), $c = 27.182$ (7) Å, $\beta = 90.78$ (3)°, $V = 1258.2$ Å³, $Z = 4$, $D_x = 1.379$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.10$ mm⁻¹, $F(000) = 544$, $T = 293$ K. Final $R = 0.055$ for 1417 unique observed reflections. The fluorine atom shows positional disorder. 2-Fluoro-2-phenylethyl 4-nitrobenzoate, (2), $C_{15}H_{12}FNO_4$, $M_r = 289.26$, orthorhombic, $P2_12_12_1$, $a = 6.0219$ (8), $b = 14.8748$ (14), $c = 15.1877$ (16) Å, $V = 1360.4$ Å³, $Z = 4$, $D_x = 1.412$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54179$ Å, $\mu = 0.91$ mm⁻¹, $F(000) = 600$, $T = 293$ K. Final $R = 0.054$ for 1851 unique observed reflections. The two related structures have closely similar conformations, with C—F *gauche* and C—Ph *anti* to the C—OX bond in each case. The C—OX bond is substantially longer in the ester [(2), 1.456 (4) Å] than in the ether [(1), 1.420 (3) Å], as expected, and shows little or no effect of the β -fluorine atom.

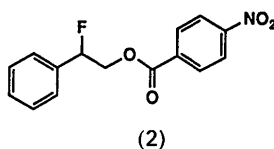
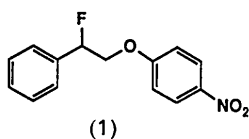
Introduction. As discussed in the previous paper (Kirby, Parker & Raithby, 1992), we wish to examine the effect on the length of the R—OX bond of the introduction of a strongly electron-withdrawing substituent on the β -carbon atom of the alkyl group R. In this paper we report our results for two derivatives of 2-fluoro-2-phenylethanol, the 4-nitrophenyl ether (1) and the 4-nitrobenzoate ester (2), compounds with a moderately poor and a moderately good leaving group XO⁻. In the following paper we

report the structures of three arenesulfonate esters of the same alcohol. (The phenyl group is present to ensure that the majority of derivatives of interest are solids under ambient conditions.)

Experimental. 2-Fluoro-2-phenylethyl 4-nitrophenyl ether (1) was prepared by arylation of the sodium salt of the parent alcohol. 2-Fluoro-2-phenylethanol [3.1 mmol, Olah & Meidar (1978)] and NaH (0.15 g, 3.3 mmol, of a 50% dispersion in mineral oil) in tetrahydrofuran were stirred under argon for 30 min at room temperature. Then tetra-*n*-butylammonium iodide (0.12 g, 0.3 mmol) and 4-fluoronitrobenzene (0.31 ml, 3.3 mmol) were added, and the mixture stirred for 4 h at 323 K. Water (50 ml) was added slowly at 273 K, the tetrahydrofuran removed *in vacuo*, and the organic layer, and subsequent CH₂Cl₂ extracts, combined and dried over MgSO₄. Purification by flash column chromatography (Merck Kieselgel 60, eluant CH₂Cl₂), and recrystallization from CH₂Cl₂–light petroleum (b.p. 313–333 K) gave the title compound as yellow prisms, m.p. 414–415 K. Crystals were grown by the vapour diffusion technique, from CH₂Cl₂–hexane.

2-Fluoro-2-phenylethyl 4-nitrobenzoate (2) was prepared by acylation of the parent alcohol in CH₂Cl₂ by the acid chloride under argon in the presence of pyridine. Purification by flash column chromatography (Merck Kieselgel 60, eluant CH₂Cl₂), and recrystallization from CH₂Cl₂–hexane, gave the title compound as colourless prisms, m.p. 372–373 K. Crystals were grown by the liquid diffusion technique, from CH₂Cl₂–light petroleum (b.p. 313–333 K).

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 $0.75 \times 0.4 \times 0.2$ [$0.7 \times 0.25 \times 0.15$] mm was mounted in a glass capillary. 3670 [2645] reflections, ($\pm h - k + l$ and some $+k$ equivalents [$+h + k + l$ and some $-h - k - l$]) were collected on a Stoe-Siemens diffractometer using monochromated Mo $K\alpha$ [Cu $K\alpha$] radiation ($2\theta_{\max}$ 50 [130]°). Three check reflections showed no significant intensity change. No absorption or extinction correction was applied. Merging equivalents gave 2207 [2214] unique reflections (R_{int} 0.021 [0.019]), index ranges after merging h 0 to 9 [0 to 6], k 0 to 6 [0 to 17], l -32 to 32 [-17 to 17], of which 1417 [1851] with $F > 4\sigma(F)$ were used for all calculations (program system Siemens *SHELXTL-Plus*; Sheldrick, 1990). Cell constants were refined from $\pm\omega$ values of 70 [52] reflections in the 2θ range 20–24 [60–65]°. The structures were solved by routine direct methods and subjected to anisotropic full-matrix least-squares refinement on F . For (1), the F atom (and therefore also the H atom) at C(2) was disordered over two sites, which were refined subject to the restraint C—F = 1.350 (5) Å; the site occupation factor refined to 0.764 (2) for the major component. H atoms were included using a riding model. The absolute structure of (2) was not determined. The final R was 0.055 [0.054], with wR 0.060 [0.059]. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0004F^2$. 177 [190] parameters; S 1.8 [1.7]; max. Δ/σ 0.005 [0.002]; max. $\Delta\rho$ +0.24, -0.27 [+0.25, -0.36] e Å⁻³.

Discussion. Final atom coordinates for (1) and (2) are given in Tables 1 and 3, and derived parameters in Tables 2 and 4, respectively.* Plots of (1) and (2), showing the atom-numbering scheme, appear as Figs. 1 and 2. In (1) the molecules are arranged in layers parallel to 101. There are non-bonded contacts < 3.24 Å between non-H atoms. In (2) the molecules are arranged in layers perpendicular to the y axis. The shortest non-bonded contacts (excluding H atoms) are O(12)⋯N(1) 2.99, F(31)⋯N(1) 3.10 Å (second atoms at $0.5 + x, 0.5 - y, -z$; $1.5 - x, 1 - y, 0.5 + z$). The shortest H⋯O contact is H(3a)⋯O(11) 2.54 Å ($-1 + x, y, z$), with C(3)⋯O(11) 3.41 Å.

The disorder of (1) implies that we are seeing a superposition of two enantiomeric forms with alternative configurations at C(2). Although the major component (76%) largely determines the observed

* 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 54752 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0052]

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for (1)

	x	y	z	U_{eq}^*
O(1)	5916 (2)	7748 (3)	4390 (1)	67 (1)
C(1)	6032 (3)	7130 (5)	3885 (1)	63 (1)
C(11)	6730 (3)	6403 (5)	4726 (1)	53 (1)
C(12)	6722 (3)	7262 (5)	5206 (1)	60 (1)
C(13)	7523 (3)	6052 (5)	5572 (1)	60 (1)
C(14)	8333 (3)	3962 (5)	5457 (1)	53 (1)
N(14)	9219 (3)	2696 (4)	5841 (1)	67 (1)
O(141)	9217 (3)	3509 (4)	6254 (1)	112 (1)
O(142)	9952 (3)	870 (4)	5739 (1)	85 (1)
C(15)	8341 (3)	3070 (5)	4986 (1)	58 (1)
C(16)	7547 (3)	4292 (5)	4619 (1)	58 (1)
C(2)	5000 (3)	8727 (5)	3589 (1)	73 (1)
F(2)	5288 (4)	11061 (4)	3679 (1)	117 (1)
F(2')	3605 (6)	9421 (13)	3762 (2)	82 (3)
C(21)	4983 (3)	8155 (5)	3052 (1)	59 (1)
C(22)	5779 (4)	9581 (6)	2724 (1)	76 (1)
C(23)	5770 (4)	9021 (6)	2231 (1)	91 (1)
C(24)	4992 (5)	7013 (7)	2065 (1)	96 (1)
C(25)	4211 (5)	5591 (6)	2388 (1)	93 (1)
C(26)	4193 (4)	6154 (6)	2878 (1)	77 (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 (°) for (1)

O(1)—C(1)	1.420 (3)	O(1)—C(11)	1.355 (3)
C(1)—C(2)	1.468 (4)	C(2)—F(2')	1.317 (6)
C(2)—F(2)	1.341 (4)	F(2)—F(2')	1.690 (7)
C(2)—C(21)	1.494 (4)		
C(11)—O(1)—C(1)	118.6 (2)	C(2)—C(1)—O(1)	109.7 (2)
C(12)—C(11)—O(1)	115.8 (2)	C(16)—C(11)—O(1)	124.5 (2)
F(2)—C(2)—C(1)	119.6 (4)	F(2)—C(2)—C(1)	112.5 (2)
C(21)—C(2)—C(1)	113.9 (2)	F(2)—C(2)—F(2')	79.0 (4)
C(21)—C(2)—F(2')	114.5 (4)	C(21)—C(2)—F(2)	112.6 (2)
F(2)—F(2)—C(2)	51.1 (2)	F(2)—F(2)—C(2)	49.9 (3)

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for (2)

	x	y	z	U_{eq}^*
C(1)	7495 (5)	3532 (2)	3849 (2)	52 (1)
C(11)	7538 (5)	3530 (2)	2869 (2)	45 (1)
C(12)	9380 (5)	3147 (2)	2463 (2)	53 (1)
C(13)	9484 (5)	3102 (2)	1557 (2)	52 (1)
C(14)	7762 (5)	3456 (2)	1080 (2)	48 (1)
C(15)	5912 (5)	3844 (2)	1463 (2)	53 (1)
C(16)	5812 (6)	3875 (2)	2368 (2)	52 (1)
N(1)	7863 (4)	3419 (2)	113 (2)	60 (1)
O(1)	5578 (4)	3854 (2)	4171 (1)	63 (1)
O(11)	8983 (4)	3269 (2)	4309 (1)	72 (1)
O(12)	9045 (4)	2858 (2)	-228 (2)	80 (1)
O(13)	6755 (5)	3955 (2)	-299 (2)	86 (1)
C(2)	5454 (6)	3843 (2)	5129 (2)	68 (1)
C(3)	3308 (6)	4258 (2)	5386 (2)	61 (1)
C(31)	2815 (5)	4142 (2)	6347 (2)	51 (1)
C(32)	843 (6)	3731 (2)	6608 (2)	61 (1)
C(33)	358 (7)	3648 (2)	7493 (3)	72 (1)
C(34)	1758 (7)	3963 (2)	8115 (2)	71 (1)
C(35)	3706 (7)	4372 (2)	7868 (2)	68 (1)
C(36)	4228 (6)	4465 (2)	6987 (2)	61 (1)
F(31)	3351 (4)	5170 (1)	5180 (1)	87 (1)

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

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

C(1)—C(11)	1.488 (4)	C(1)—O(1)	1.342 (4)
C(1)—O(11)	1.202 (4)	C(2)—C(3)	1.484 (5)
O(1)—C(2)	1.456 (4)	C(3)—F(31)	1.393 (4)
C(3)—C(31)	1.500 (4)		
O(1)—C(1)—C(11)	112.4 (2)	O(11)—C(1)—C(11)	124.6 (3)
O(11)—C(1)—O(1)	123.0 (3)	C(12)—C(11)—C(1)	117.3 (3)
C(16)—C(11)—C(1)	122.3 (3)	C(3)—C(2)—O(1)	107.6 (3)
C(2)—O(1)—C(1)	113.9 (2)	F(31)—C(3)—C(2)	109.2 (3)
C(31)—C(3)—C(2)	112.3 (3)	C(32)—C(31)—C(3)	119.7 (3)
F(31)—C(3)—C(31)	109.5 (3)	C(36)—C(31)—C(3)	121.6 (3)

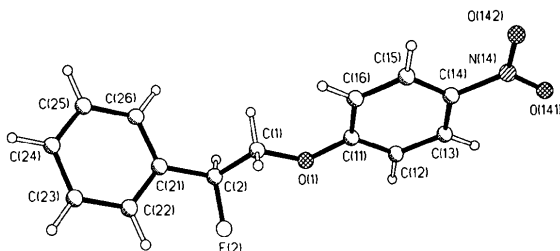


Fig. 1. Molecular structure of (1), showing the atom-numbering scheme. There is positional H/F disorder at C(2): only the major component is shown.

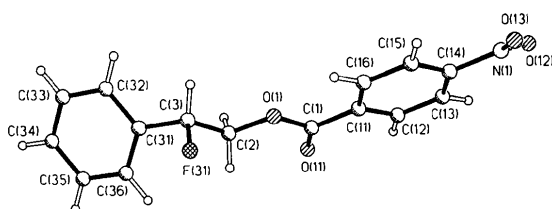


Fig. 2. Molecular structure of (2), showing the atom-numbering scheme.

bond lengths, they should clearly be interpreted with some caution; however, the normal temperature factors indicate that no more severe disorder is present. The H/F disorder proves to be a frequent feature of this series of compounds; it is less frequent in non-centrosymmetric structures [no disorder is observed

in (2), where the enantiomers seem well resolved between crystals].

The conformations of the two compounds are similar in the crystal, with the phenyl ring *anti* and the C—F bond close to *gauche* to the C—O bond [torsion angles O(1)—C(1)—C(2)—C(21 or 31) 177.1 (4) and 52.8 (4)°, and 170.1 (4) and 68.1 (4)° for (1) and (2), respectively]. This is the expected conformation, determined, with respect to the C—OX bond, by the steric bulk of the phenyl group and the electronic (*gauche*) effect of the fluorine. The C—OAr bond length in (1) is 1.420 (3) Å, shorter than expected for a bond from primary C to 4-nitrophenol. [Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) give a mean value of 1.431 (13) Å for all types of aryloxy group, and we reported a mean value of 1.437 (3) Å for 32 compounds with only C or H atoms at the β -position (Allen & Kirby, 1984).]

On the other hand, the C—O acyl bond length in (2), at 1.456 (4) Å, is no shorter than expected for an alkyl ester bond at a primary centre. Here the literature values are in agreement, 1.452 (9) Å for all esters (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), 1.452 (2) Å for the subset with only C—H or CC bonds β to the O acyl bond (Allen & Kirby, 1984). Thus the present data allow no clear conclusion about the effect of the *gauche* F atom on the length of the C—OX bond.

We thank the Fonds der Chemischen Industrie for support.

References

- ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- ALLEN, F. H. & KIRBY, A. J. (1984). *J. Am. Chem. Soc.* **106**, 6197–6200.
- KIRBY, A. J., PARKER, J. K. & RAITHBY, P. R. (1992). *Acta Cryst. C* **48**, 832–834.
- OLAH, G. & MEIDAR, D. (1978). *Isr. J. Chem.* **17**, 148–149.
- SHELDRIK, G. M. (1990). *SHELXTL Users Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.