

are very slightly longer for larger torsion angles for the benzyl esters [1.451 (11) Å for $abd < 30^\circ$, 1.459 (14) Å for abd between $70\text{--}80^\circ$]; and perhaps shorter for ethers (histograms *C* and *D*) than esters, though the differences are less than the sum of the standard deviations. The data for compounds (1) and (2) fall in the ranges expected from the trends suggested by these histograms.

We thank the Fonds der Chemischen Industrie, and the Cambridge Philosophical Society, for support.

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Acta Cryst. (1989). **C45**, 237–239

Bond Length and Reactivity.* Structure of 3,5-Bis(trifluoromethyl)benzyl 4-Nitrobenzoate

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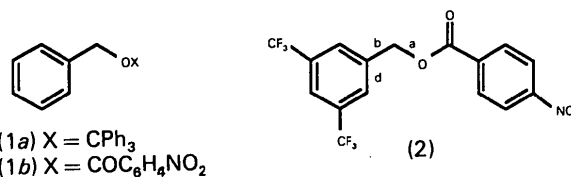
(Received 7 July 1988; accepted 16 August 1988)

Abstract. $C_{16}H_9F_6NO_4$, $M_r = 393.24$, triclinic, $P\bar{1}$, $a = 8.500$ (1), $b = 9.683$ (1), $c = 10.120$ (1) Å, $\alpha = 86.96$ (1), $\beta = 77.19$ (1), $\gamma = 82.19$ (1)°, $V = 804.4$ Å³, $Z = 2$, $D_x = 1.62$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 1.3$ mm⁻¹, $F(000) = 396$, $T = 293$ K, $R = 0.060$ for 2623 unique observed reflections. The molecule is almost planar. In particular the C–O acyl bond is within 5° of being coplanar with the aromatic ring. As a result this bond is significantly shorter than that of the same ester of 2,6-dimethylbenzyl alcohol.

Introduction. We have reported crystal structures for two representative benzyl compounds, the triphenylmethyl ether (1*a*) and the *p*-nitrobenzoate ester (1*b*), and shown how they fit into the trends established by published structures of derivatives of benzyl alcohol (Jones, Dölle, Kirby & Parker, 1989*b*). We report here the structure of 3,5-bis(trifluoromethyl)benzyl *p*-nitrobenzoate (2), an ester with two strongly electron-withdrawing groups in the ring.

* Previous paper in this series: Jones, Dölle, Kirby & Parker (1989*b*).

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Experimental. The ester was prepared by acylation of the lithium salt of the alcohol using 4-nitrobenzoyl chloride. It was recrystallized by diffusion of hexane into a solution in dichloromethane, to give yellow blocks, m.p. 371–373 K.

A crystal $0.7 \times 0.45 \times 0.35$ mm, cut from a larger block, was mounted in a glass capillary. A complete sphere of profile-fitted data (Clegg, 1981) to $2\theta_{\max} = 135^\circ$ was measured on a Stoe–Siemens four-circle diffractometer using monochromated Cu $K\alpha$ radiation. No crystal decay was observed on monitoring three check reflections, and no corrections for absorption or extinction were carried out. Cell constants were refined from 2θ values of 66 reflections in the range $55\text{--}65^\circ$.

Of 5617 measured reflections, 2812 were unique ($R_{\text{int}} = 0.037$) and 2623 with $F > 4\sigma(F)$ considered observed. Index ranges after merging: $h -9$ to 9 , $k -11$ to 11 , $l 0$ to 12 .

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

	x	y	z	U_{eq} *
C(1)	1346 (3)	5480 (3)	1389 (3)	76 (1)
C(2)	3229 (3)	3879 (3)	30 (2)	65 (1)
O(1)	2791 (2)	4479 (2)	1247 (2)	69 (1)
O(2)	2516 (3)	4183 (2)	-857 (2)	98 (1)
C(11)	965 (3)	6116 (3)	2772 (2)	63 (1)
C(12)	1960 (3)	5850 (2)	3692 (2)	63 (1)
C(13)	1526 (3)	6521 (2)	4939 (2)	61 (1)
C(14)	119 (3)	7444 (2)	5253 (2)	65 (1)
C(15)	-871 (3)	7689 (2)	4334 (2)	63 (1)
C(16)	-443 (3)	7035 (3)	3094 (2)	65 (1)
C(17)	2638 (3)	6261 (3)	5912 (3)	78 (1)
F(1)	3274 (2)	4950 (2)	5981 (2)	99 (1)
F(2)	1890 (3)	6608 (3)	7166 (2)	134 (1)
F(3)	3881 (3)	6982 (2)	5560 (3)	128 (1)
C(18)	-2387 (4)	8704 (3)	4661 (3)	81 (1)
F(4)	-3293 (3)	8438 (3)	5893 (3)	123 (1)
F(5)	-3373 (3)	8703 (3)	3847 (2)	123 (1)
F(6)	-2072 (3)	9964 (3)	4792 (6)	159 (2)
F(4A)	-2297 (30)	9773 (20)	3738 (22)	112 (6)
F(5A)	-2533 (34)	9467 (25)	5714 (19)	112 (6)
F(6A)	-3682 (20)	8085 (23)	5211 (27)	112 (6)
C(21)	4654 (3)	2785 (2)	-76 (2)	60 (1)
C(22)	5371 (3)	2356 (3)	999 (2)	70 (1)
C(23)	6630 (3)	1260 (3)	856 (3)	76 (1)
C(24)	7134 (3)	640 (3)	-391 (3)	70 (1)
C(25)	6477 (3)	1075 (3)	-1482 (3)	79 (1)
C(26)	5232 (3)	2159 (3)	-1337 (2)	73 (1)
N(1)	8419 (3)	-581 (3)	-520 (3)	90 (1)
O(3)	8943 (4)	-1046 (4)	-1634 (3)	161 (2)
O(4)	8869 (3)	-1044 (3)	470 (3)	111 (1)

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

The structure was solved by routine direct methods and subjected to full-matrix least-squares refinement on F using program system *SHELX76* (Sheldrick, 1976) locally modified by its author. Non-H atoms were refined anisotropically, H atoms isotropically using a riding model. The CF_3 group involving F(4-6) was disordered over two sites, with refined site occupancies of 0.9, 0.1. The minor component F(4A-6A) was refined isotropically with a common temperature factor, and subject to the restraint $\text{C}-\text{F} = 1.35 (1) \text{\AA}$. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$. An extinction correction of the form $F_{\text{corr}} = F_c / (1 + xF_c^2 / \sin 2\theta)^{0.25}$ was applied; x refined to $1.0 (1) \times 10^{-4}$. The final R value was 0.060 for 256 parameters, with $wR = 0.100$, $S = 6.3$, max. $\Delta/\sigma = 0.4$, max. $\Delta\rho$ within $\pm 0.33 \text{ e \AA}^{-3}$. We suspect that the high S and wR values may be associated with inappropriate estimates of $\sigma(I)$ for strong reflections; some time after this data collection the program was modified and the problem no longer occurred. Atomic scattering factors from *SHELX76*.*

* Lists of H-atom coordinates and U_{iso} values, structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51336 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Molecular geometry of (2): bond lengths (\AA) and bond angles ($^\circ$)

C(1)-O(1)	1.443 (3)	C(1)-C(11)	1.510 (3)
C(2)-O(1)	1.344 (3)	C(2)-O(2)	1.193 (3)
C(2)-C(21)	1.486 (3)	C(11)-C(12)	1.383 (3)
C(11)-C(16)	1.378 (3)	C(12)-C(13)	1.403 (3)
C(13)-C(14)	1.379 (3)	C(13)-C(17)	1.499 (3)
C(14)-C(15)	1.378 (3)	C(15)-C(16)	1.388 (3)
C(15)-C(18)	1.496 (4)	C(17)-F(1)	1.314 (3)
C(17)-F(2)	1.325 (3)	C(17)-F(3)	1.318 (4)
C(18)-F(4)	1.345 (4)	C(18)-F(5)	1.300 (3)
C(18)-F(6)	1.304 (4)	C(18)-F(4A)	1.356 (9)
C(18)-F(5A)	1.303 (9)	C(18)-F(6A)	1.324 (9)
C(21)-C(22)	1.379 (3)	C(21)-C(26)	1.400 (3)
C(22)-C(23)	1.390 (4)	C(23)-C(24)	1.381 (3)
C(24)-C(25)	1.366 (4)	C(24)-N(1)	1.487 (4)
C(25)-C(26)	1.374 (4)	N(1)-O(3)	1.204 (3)
N(1)-O(4)	1.194 (3)		
C(11)-C(1)-O(1)	109.7 (2)	O(2)-C(2)-O(1)	122.9 (2)
C(21)-C(2)-O(1)	113.1 (2)	C(21)-C(2)-O(2)	124.0 (2)
C(2)-O(1)-C(1)	113.5 (2)	C(12)-C(11)-C(1)	123.7 (2)
C(16)-C(11)-C(1)	116.7 (2)	C(16)-C(11)-C(12)	119.6 (2)
C(13)-C(12)-C(11)	119.6 (2)	C(14)-C(13)-C(12)	120.5 (2)
C(17)-C(13)-C(12)	119.2 (2)	C(17)-C(13)-C(14)	120.2 (2)
C(15)-C(14)-C(13)	119.3 (2)	C(16)-C(15)-C(14)	120.5 (2)
C(18)-C(15)-C(14)	119.5 (2)	C(18)-C(15)-C(16)	120.0 (2)
C(15)-C(16)-C(11)	120.5 (2)	F(1)-C(17)-C(13)	113.4 (2)
F(2)-C(17)-C(13)	112.3 (2)	F(2)-C(17)-F(1)	106.3 (2)
F(3)-C(17)-C(13)	111.4 (2)	F(3)-C(17)-F(1)	105.8 (2)
F(3)-C(17)-F(2)	107.1 (2)	F(4)-C(18)-C(15)	111.7 (3)
F(5)-C(18)-C(15)	115.2 (2)	F(5)-C(18)-F(4)	104.3 (3)
F(6)-C(18)-C(15)	112.0 (2)	F(6)-C(18)-F(4)	101.9 (3)
F(6)-C(18)-F(5)	110.7 (3)	F(4A)-C(18)-C(15)	109.6 (11)
F(5A)-C(18)-C(15)	115.8 (12)	F(6A)-C(18)-C(15)	112.3 (11)
C(22)-C(21)-C(2)	123.2 (2)	C(26)-C(21)-C(2)	116.4 (2)
C(26)-C(21)-C(22)	120.4 (2)	C(23)-C(22)-C(21)	120.3 (2)
C(24)-C(23)-C(22)	117.7 (2)	C(25)-C(24)-C(23)	123.0 (2)
N(1)-C(24)-C(23)	117.5 (2)	N(1)-C(24)-C(25)	119.4 (2)
C(26)-C(25)-C(24)	119.1 (2)	C(25)-C(26)-C(21)	119.4 (2)
O(3)-N(1)-C(24)	117.1 (3)	O(4)-N(1)-C(24)	119.0 (3)
O(4)-N(1)-O(3)	123.9 (3)		

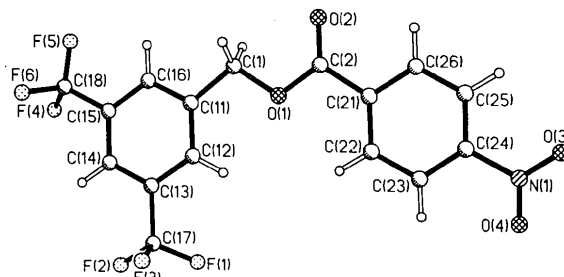


Fig. 1. Molecular structure of (2), showing the atom-numbering scheme.

Discussion. Final atom coordinates and derived parameters are presented in Tables 1 and 2 and a plot of (2) is shown in Fig. 1. The atom-numbering scheme in the benzylic system is the same as for previous compounds in this series.

The ester (2) crystallizes in an extended, almost planar conformation: none of the torsion angles is greater than $5.4 (4)^\circ$. This is expected for the ester group, and common for the torsion angle about C(1)-O(1), and we have pointed out (Jones, Dölle, Kirby & Parker, 1989b), that *p*-nitrobenzyl esters show

a preference for a small torsion angle abd . The two *meta*-CF₃ groups ($\sigma_m = 0.415$, Jaffé, 1953) represent together more powerful electron withdrawal than that due to a single *p*-nitro group, so the low torsion angle abd , and a relatively short bond a [$5.4(4)^\circ$ and $1.443(3) \text{ \AA}$, respectively] are expected.

We have thus defined conditions for controlling the conformation of the C—OX bond of benzyl alcohol derivatives without the need for synthesizing structures of fixed conformation. Introducing strongly electron-withdrawing substituents into the aromatic ring generates a preference for coplanarity with the ring, as in compound (2): whereas the C—OX bond can be directed into a near-perpendicular conformation by introducing two *ortho*-methyl groups (Jones, Dölle, Kirby & Parker, 1989a). There is already good evidence that the length of the C—O bond a depends on the torsion angle abd , as shown previously for 1-arylethanol derivatives (Edwards, Jones & Kirby, 1986). This work produces a clear-cut example of this

effect: the C—OCOAr bond length a and torsion angle abd of $1.443(3) \text{ \AA}$ and $5.4(4)^\circ$ for (2) compare with values of $1.467(2) \text{ \AA}$ and $86.3(2)^\circ$ for molecule *B* of the *p*-nitrobenzoate of 2,6-dimethylbenzyl alcohol (Jones *et al.*, 1989a).

We thank the Fonds der Chemischen Industrie, and the Cambridge Philosophical Society, for support.

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Acta Cryst. (1989). **C45**, 239–241

Bond Length and Reactivity.* Structure of 2-(4-Nitrophenoxy)tetrahydrofuran

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(Received 18 July 1988; accepted 21 September 1988)

Abstract. C₁₀H₁₁NO₄, $M_r = 209.20$, monoclinic, $P2_1/c$, $a = 9.767(2)$, $b = 11.942(2)$, $c = 8.522(2) \text{ \AA}$, $\beta = 92.06(2)^\circ$, $V = 993.4 \text{ \AA}^3$, $Z = 4$, $D_x = 1.40 \text{ Mg m}^{-3}$, $F(000) = 440$, $\lambda(\text{MoK}\alpha) = 0.71069 \text{ \AA}$, $\mu = 0.1 \text{ mm}^{-1}$, $T = 293 \text{ K}$. The structure was refined to $R = 0.052$ for 1531 unique observed reflections. The tetrahydrofuran ring adopts a distorted envelope conformation commonly observed for the ribose ring of nucleosides and nucleotides. The acetal C—O bond lengths differ, with the exocyclic bond C(2)—O(2) = $1.439(3) \text{ \AA}$ longer than the endocyclic C(2)—O(1) = $1.392(3) \text{ \AA}$. Both are closely similar to those observed for a comparable tetrahydropyranyl acetal.

Introduction. We have demonstrated linear relationships between bond length and reactivity in several series of acetals (Jones & Kirby, 1979, 1984, 1986; Briggs, Glenn, Jones, Kirby & Ramaswamy, 1984). As a general rule, the longer the C—O bond in a given series, the faster it breaks: furthermore, the more reactive the system, the more sensitive is the length of the bond that breaks to the leaving group capability of the group OX (Jones & Kirby, 1984). The most reactive, and most sensitive, of the systems we have studied are the tetrahydropyranyl acetals, which favour the axial conformation (1), both in solution and in the solid state. This is a manifestation of the anomeric effect (Kirby, 1983).

* Crystal Structures of Acetals. 26. Part 25: Jones, Sheldrick, Kirby & Briggs (1985).

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