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

References

Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.

Dölle, A. (1988). Diplomarbeit. Univ. of Göttingen, Federal Republic of Germany.

Edwards, M. R., Jones, P. G. & Kirby, A. J. (1986). *J. Am. Chem. Soc.* **108**, 7067–7073.

Gilmore, C. J. & Brown, S. R. (1988). *Acta Cryst.* A**44**, 1018–1021.

Jones, P. G. (1984). *Acta Cryst.* A**40**, 660–662.

Jones, P. G., Dölle, A., Kirby, A. J. & Parker, J. K. (1989). *Acta Cryst.* C**45**, 226–230.

Rogers, D. (1981). *Acta Cryst.* A**37**, 734–741.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination and refinement. Univs. of Cambridge, England, and Göttingen, Federal Republic of Germany.

Taft, R. W. (1956). In *Steric Effects in Organic Chemistry*, edited by M. S. Newman, p. 598. New York: John Wiley.

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Bond Length and Reactivity.* Structures of the Triphenylmethyl Ether and the 4-Nitrobenzoate Ester of Benzyl Alcohol

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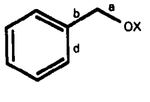
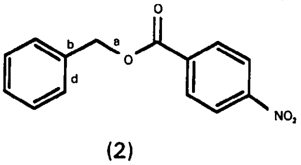
Abstract. Benzyl triphenylmethyl ether (1), $C_{26}H_{22}O$, $M_r = 350·46$, monoclinic, $P2_1/n$, $a = 9·539\,(2)$, $b = 10·681\,(2)$, $c = 19·680\,(3)$ Å, $\beta = 101·29\,(2)°$, $V = 1966·3$ Å^3, $Z = 4$, $D_x = 1·18$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·07$ mm^{-1}, $F(000) = 744$, $T = 293$ K, $R = 0·053$ for 3561 unique observed reflections. Benzyl 4-nitrobenzoate (2), $C_{14}H_{11}NO_4$, $M_r = 257·25$, monoclinic, $P2_1/n$, $a = 6·180\,(2)$, $b = 7·717\,(2)$, $c = 26·277\,(6)$ Å, $\beta = 93·02\,(2)°$, $V = 1251·3$ Å^3, $Z = 4$, $D_x = 1·37$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·09$ mm^{-1}, $F(000) = 536$, $T = 293$ K, $R = 0·053$ for 2188 observed reflections. C—OX bond lengths [1·420 (3), 1·454 (3) Å] are similar to those in the corresponding derivatives of 2,6-dimethyl [1·444 (3), av. 1·462 (5) Å] and 2,6-dichlorobenzyl [1·425 (3), 1·467 (4) Å] alcohols, but the ring—C—O torsion angles no longer lie close to 90° [O(1)—C(2)—C(21)—C(26) = 39·2 (4), 47·0 (4)° for (1) and (2), respectively].

Introduction. We have reported structures of three derivatives each of 2,6-dimethyl and 2,6-dichlorobenzyl alcohols (Jones, Dölle, Kirby & Parker, 1989*a*,*b*). These were found, as expected, to favour conformations in which the benzylic C—OX bond *a* is perpendicular to the plane of the aromatic ring. We report here structures of two simple benzyl derivatives, the triphenylmethyl ether (1) and the *p*-nitrobenzoate ester (2) bearing two of the leaving groups used in this work. Structures are available for a large number of ArCH$_2$OX compounds – a search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) in June 1987 retrieved 230 structures – but as is inevitably the case, these represent a very disparate set of compounds. The largest groups are esters and carbamate esters of α-amino acids, the great majority of which have acidic (NH or OH) groups, which can perturb bond-length correlations by hydrogen bonding. The same is true of the ethers. When such compounds are omitted, and structures with $R < 7\%$ screened out (Allen & Kirby, 1984) only a handful of structures remain. In particular, neither the triphenylmethyl ether nor the *p*-nitrobenzoate ester leaving group has been studied in this system.



(1) X = CPh$_3$



(2)

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

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* (Å^2 $\times$ 10^3)

	x	y	z	U_{eq}*
(*a*) Compound (1)				
O(1)	5687 (1)	5285 (1)	3346 (1)	53 (1)
C(1)	6278 (1)	4124 (1)	3150 (1)	48 (1)
C(111)	7795 (1)	3980 (1)	3577 (1)	55 (1)
C(112)	8903 (1)	4635 (2)	3378 (1)	74 (1)
C(113)	10257 (2)	4614 (2)	3788 (1)	103 (1)
C(114)	10521 (2)	3951 (2)	4396 (1)	108 (1)
C(115)	9432 (2)	3323 (2)	4604 (1)	92 (1)
C(116)	8072 (2)	3332 (1)	4197 (1)	68 (1)
C(121)	6277 (1)	4262 (1)	2372 (1)	52 (1)
C(122)	6953 (2)	3376 (2)	2037 (1)	73 (1)
C(123)	6918 (2)	3458 (2)	1333 (1)	89 (1)
C(124)	6204 (2)	4425 (2)	955 (1)	86 (1)
C(125)	5525 (2)	5300 (2)	1280 (1)	75 (1)
C(126)	5565 (1)	5228 (1)	1986 (1)	59 (1)
C(131)	5265 (1)	3031 (1)	3214 (1)	47 (1)
C(132)	5712 (1)	1792 (1)	3242 (1)	57 (1)
C(133)	4746 (2)	819 (1)	3231 (1)	65 (1)
C(134)	3322 (2)	1072 (2)	3198 (1)	67 (1)
C(135)	2864 (2)	2291 (2)	3176 (1)	67 (1)
C(136)	3820 (1)	3261 (1)	3177 (1)	56 (1)
C(2)	5692 (2)	5441 (1)	4063 (1)	60 (1)
C(21)	4814 (1)	6562 (1)	4167 (1)	52 (1)
C(22)	5240 (2)	7323 (1)	4738 (1)	65 (1)
C(23)	4411 (2)	8331 (2)	4859 (1)	81 (1)
C(24)	3151 (2)	8583 (2)	4414 (1)	83 (1)
C(25)	2722 (2)	7846 (2)	3844 (1)	77 (1)
C(26)	3547 (2)	6847 (2)	3720 (1)	65 (1)
(*b*) Compound (2)				
O(1)	3391 (2)	4148 (2)	6382 (1)	70 (1)
C(1)	2349 (2)	4180 (2)	5928 (1)	59 (1)
O(11)	590 (2)	4816 (2)	5852 (1)	92 (1)
C(11)	3615 (2)	3386 (2)	5522 (1)	52 (1)
C(12)	5701 (2)	2748 (2)	5616 (1)	56 (1)
C(13)	6820 (2)	2039 (2)	5226 (1)	57 (1)
C(14)	5824 (2)	1994 (2)	4745 (1)	52 (1)
N(14)	7004 (2)	1246 (2)	4326 (1)	65 (1)
O(141)	6123 (2)	1240 (2)	3901 (1)	99 (1)
O(142)	8807 (2)	652 (2)	4423 (1)	89 (1)
C(15)	3761 (2)	2624 (2)	4640 (1)	59 (1)
C(16)	2667 (2)	3313 (2)	5031 (1)	59 (1)
C(2)	2301 (3)	4955 (3)	6798 (1)	74 (1)
C(21)	3959 (2)	5299 (2)	7221 (1)	55 (1)
C(22)	5916 (3)	6063 (2)	7127 (1)	66 (1)
C(23)	7429 (3)	6393 (3)	7517 (1)	77 (1)
C(24)	7011 (4)	5968 (3)	8005 (1)	89 (1)
C(25)	5057 (4)	5247 (3)	8108 (1)	89 (1)
C(26)	3526 (3)	4900 (2)	7717 (1)	69 (1)

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

Table 2. *Molecular geometry for* (1) *and* (2): *bond lengths* (Å) *and bond angles* (°)

(*a*) Compound (1)			
O(1)–C(1)	1·446 (1)	O(1)–C(2)	1·420 (2)
C(1)–C(111)	1·532 (2)	C(1)–C(121)	1·537 (2)
C(1)–C(131)	1·536 (2)	C(111)–C(112)	1·386 (2)
C(111)–C(116)	1·382 (2)	C(112)–C(113)	1·384 (2)
C(113)–C(114)	1·371 (3)	C(114)–C(115)	1·365 (3)
C(115)–C(116)	1·385 (2)	C(121)–C(122)	1·384 (2)
C(121)–C(126)	1·379 (2)	C(122)–C(123)	1·380 (2)
C(123)–C(124)	1·374 (3)	C(124)–C(125)	1·366 (3)
C(125)–C(126)	1·385 (2)	C(131)–C(132)	1·388 (2)
C(131)–C(136)	1·388 (2)	C(132)–C(133)	1·387 (2)
C(133)–C(134)	1·374 (2)	C(134)–C(135)	1·371 (2)
C(135) C(136)	1·379 (2)	C(2) C(21)	1·498 (2)
C(21)–C(22)	1·382 (2)	C(21)–C(26)	1·383 (2)
C(22)–C(23)	1·383 (2)	C(23)–C(24)	1·367 (2)
C(24)–C(25)	1·366 (3)	C(25)–C(26)	1·376 (2)
C(2)–O(1)–C(1)	116·1 (1)	C(111)–C(1)–O(1)	108·4 (1)
C(121)–C(1)–O(1)	105·0 (1)	C(121)–C(1)–C(111)	111·9 (1)
C(131)–C(1)–O(1)	110·1 (1)	C(131)–C(1)–C(111)	114·9 (1)
C(131)–C(1)–C(121)	106·1 (1)	C(112)–C(111)–C(1)	119·0 (1)
C(116)–C(111)–C(1)	122·1 (1)	C(116)–C(111)–C(112)	118·5 (1)
C(113)–C(112)–C(111)	120·2 (2)	C(114)–C(113)–C(112)	120·6 (2)
C(115)–C(114)–C(113)	119·7 (2)	C(116)–C(115)–C(114)	120·3 (2)
C(115)–C(116)–C(111)	120·7 (2)	C(122)–C(121)–C(1)	120·0 (1)
C(126)–C(121)–C(1)	121·7 (1)	C(126)–C(121)–C(122)	118·3 (1)
C(123)–C(122)–C(121)	120·8 (1)	C(124)–C(123)–C(122)	120·3 (2)
C(125)–C(124)–C(123)	119·4 (2)	C(126)–C(125)–C(124)	120·7 (2)
C(125)–C(126)–C(121)	120·6 (1)	C(132)–C(131)–C(1)	122·2 (1)
C(136)–C(131)–C(1)	119·8 (1)	C(136)–C(131)–C(132)	117·7 (1)
C(133)–C(132)–C(131)	121·0 (1)	C(134)–C(133)–C(132)	120·1 (1)
C(135)–C(134)–C(133)	119·6 (1)	C(136)–C(135)–C(134)	120·4 (1)
C(135)–C(136)–C(131)	121·1 (1)	C(21)–C(2)–O(1)	109·6 (1)
C(22)–C(21)–C(2)	119·8 (1)	C(26)–C(21)–C(2)	122·2 (1)
C(26)–C(21)–C(22)	118·0 (1)	C(23)–C(22)–C(21)	120·7 (1)
C(24)–C(23)–C(22)	120·2 (2)	C(25)–C(24)–C(23)	119·8 (2)
C(26)–C(25)–C(24)	120·2 (2)	C(25)–C(26)–C(21)	121·1 (1)
(*b*) Compound (2)			
O(1)–C(1)	1·325 (2)	O(1)–C(2)	1·454 (2)
C(1)–O(11)	1·200 (2)	C(1)–C(11)	1·487 (2)
C(11)–C(12)	1·390 (2)	C(11)–C(16)	1·389 (2)
C(12)–C(13)	1·379 (2)	C(13)–C(14)	1·377 (2)
C(14)–N(14)	1·470 (2)	C(14)–C(15)	1·378 (2)
N(14)–O(141)	1·216 (2)	N(14)–O(142)	1·218 (2)
C(15)–C(16)	1·367 (2)	C(2)–C(21)	1·496 (2)
C(21)–C(22)	1·380 (2)	C(21)–C(26)	1·378 (2)
C(22)–C(23)	1·375 (3)	C(23)–C(24)	1·361 (3)
C(24)–C(25)	1·370 (3)	C(25)–C(26)	1·386 (3)
C(1)–O(1)–C(2)	116·5 (1)	O(1)–C(1)–O(11)	123·4 (2)
O(1)–C(1)–C(11)	112·8 (1)	O(11)–C(1)–C(11)	123·8 (1)
C(1)–C(11)–C(12)	122·5 (1)	C(1)–C(11)–C(16)	118·0 (1)
C(12)–C(11)–C(16)	119·5 (1)	C(11)–C(12)–C(13)	120·3 (1)
C(12)–C(13)–C(14)	118·4 (1)	C(13)–C(14)–N(14)	118·8 (1)
C(13)–C(14)–C(15)	122·5 (1)	N(14)–C(14)–C(15)	118·7 (1)
C(14)–N(14)–O(141)	118·2 (1)	C(14)–N(14)–O(142)	118·4 (1)
O(141)–N(14)–O(142)	123·4 (2)	C(14)–C(15)–C(16)	118·5 (1)
C(11)–C(16)–C(15)	120·8 (1)	O(1)–C(2)–C(21)	108·0 (1)
C(2)–C(21)–C(22)	121·0 (1)	C(2)–C(21)–C(26)	120·2 (1)
C(22)–C(21)–C(26)	118·7 (1)	C(21)–C(22)–C(23)	120·9 (2)
C(22)–C(23)–C(24)	120·2 (2)	C(23)–C(24)–C(25)	119·7 (2)
C(24)–C(25)–C(26)	120·5 (2)	C(21)–C(26)–C(25)	119·9 (2)

Experimental. The compounds were prepared as described for other benzylic ethers and esters (Jones *et al.*, 1989*a*,*b*). The ether (1) gave colourless blocks, m.p. 357–359 K, on diffusing hexane vapour into a solution in dichloromethane. The ester (2) formed yellow platelets, m.p. 379–380 K, under the same conditions.

Crystals were mounted in glass capillaries; intensities were registered on a Stoe–Siemens four-circle diffractometer in profile-fitting mode (Clegg, 1981) using monochromated Mo $K\alpha$ radiation. No corrections for crystal decay, absorption or extinction were necessary (monitoring three check reflections). Cell constants were refined from 2θ values of selected strong reflections [74, 72 for (1) and (2), respectively] in the range 20–25°.

(1), crystal 0·8 × 0·6 × 0·5 mm, 8996 reflections to $2\theta_{max} = 55°$ (one complete hemisphere), 4502 unique ($R_{int} = 0{\cdot}013$, index ranges h −12 to 12, k 0 to 13, l 0 to 25), 3561 with $F > 4\sigma(F)$. (2), crystal size 0·7 × 0·7 × 0·2 mm, 5497 reflections to $2\theta_{max} = 55°$ (complete hemisphere), 2828 unique ($R_{int} = 0{\cdot}015$, index ranges h −8 to 8, k 0 to 10, l 0 to 34), 2188 observed.

Calculations were performed with the program system *SHELX76* (Sheldrick, 1976), locally modified by its author. The stuctures were solved by routine direct methods and subjected to full-matrix least-squares refinement. All non-H atoms were refined anisotropically, H isotropically using a riding model. Weighting schemes $w^{-1} = \sigma^2(F) + gF^2$ were employed. (1): $R = 0{\cdot}053$, $wR = 0{\cdot}057$, 244 parameters, $S = 2{\cdot}5$,

$g = 0.0002$, max. $\Delta/\sigma = 0.003$, max. $\Delta\rho$ within ± 0.15 e Å^{-3}. (2): 172 parameters, $R = 0.053$, $wR = 0.061$, $S = 2.2$, $g = 0.0003$, max. $\Delta/\sigma = 0.003$, max. $\Delta\rho$ within ± 0.15 e Å^{-3}. Atomic scattering factors from *SHELX*76.*

Discussion. Final atom coordinates are presented in Table 1, and derived parameters in Table 2. Plots of (1) and (2), showing the atom-numbering schemes, appear in Fig. 1.

Both compounds crystallize in extended conformations, close to antiperiplanar about O(1)—C(2) [torsion angles −169·6 (4) and −161·9 (4)°, respectively]. The C—O bond length *a* of the ether (1) is 1·420 (3) Å, similar to that in the corresponding 2,6-dichlorobenzyl ether [1·425 (3) Å (Jones *et al.*, 1989*b*)], but shorter than that in the corresponding 2,6-dimethylbenzyl ether [1·444 (3) Å (Jones *et al.*, 1989*a*)]; consistent with a possible steric effect on this bond length in the latter compound, though the evidence is far from conclusive. The C—O bond length *a* in (2) is 1·454 (3) Å, similar to the corresponding bonds in the 2,6-dimethyl [two molecules, 1·458 (2) and 1·467 (2) Å] and 2,6-dichlorobenzyl [3,5-dinitrobenzoate, 1·467 (4) Å] esters studied previously (Jones *et al.*, 1989*a*,*b*), though the dihedral angle *abd*, like that of the triphenylmethyl ether (1), is no longer constrained to be close to 90° [39·2 (4) and 47·0 (4)° in (1) and (2), respectively].

A detailed analysis of structures of simple benzyl compounds available in the literature is not justified, because of the wide variety of the compounds involved and the expected complications from hydrogen bonding, but some trends are discernible. Fig. 2 illustrates relationships between C—O bond length *a* and dihedral angle *abd* for several sets of compounds. Histograms *A* and *B* summarize data for α-amino acid esters. The data for unsubstituted benzyl esters (*A*) suggest a modest preference for torsion angles closer to perpendicular; for only four of 18 compounds is *abd* < 40°: whereas seven out of ten *p*-nitrobenzyl esters have this angle < 20°. This is consistent with a reduction in the strength of the π–σ^* C—O*X* orbital interaction (maximal at *abd* = 90°), caused by the introduction of the electron-withdrawing *p*-nitro group. Consistent with this interpretation, mean bond lengths *a*

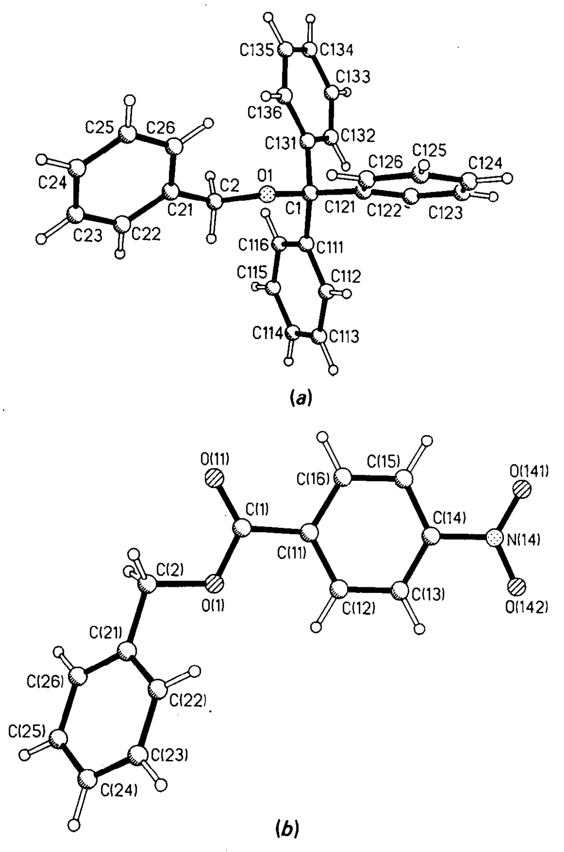

Fig. 1. (*a*) Molecular structure of (1), showing the atom-numbering scheme. (*b*) Molecular structure of (2), showing the atom-numbering scheme.

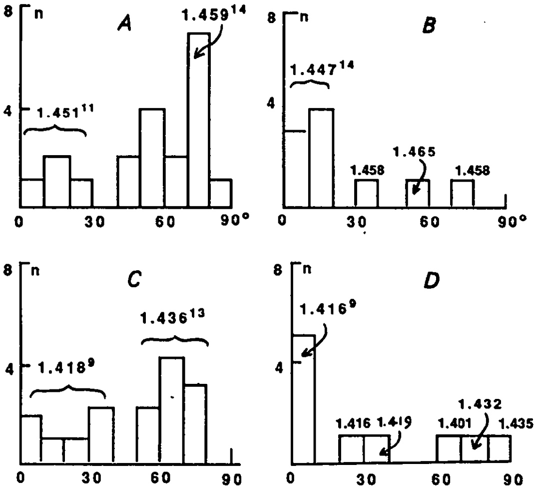

Fig. 2. Histograms representing distribution of dihedral angles *abd* (°) in benzyl derivatives. *A*, *B* for benzyl and *p*-nitrobenzyl esters, respectively, *C* and *D* for ethers with and without electron-withdrawing substituents. Set *C* refers to alkyl benzyl ethers, set *D* to aryl ethers with electron-withdrawing substituents in the benzyl ring. Mean C—O*X* bond lengths, with sample standard deviations superscripted, are shown for the data sets specified. Other figures represent individual C—O*X* bond lengths. Data were retrieved from the Cambridge Structural Database (Allen *et al.*, 1983).

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* Lists of H-atom coordinates and $U_{\rm iso}$ values, structure factors, torsion angles and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51334 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

are very slightly longer for larger torsion angles for the benzyl esters [1·451 (11) Å for *abd* < 30°, 1·459 (14) Å for *abd* between 70–80°]; 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.

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References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–152.

Allen, F. H. & Kirby, A. J. (1984). *J. Am. Chem. Soc.* **106**, 6197–6200.

Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.

Jones, P. G., Dölle, A., Kirby, A. J. & Parker, J. K. (1989*a*). *Acta Cryst.* C**45**, 226–230.

Jones, P. G., Dölle, A., Kirby, A. J. & Parker, J. K. (1989*b*). *Acta Cryst.* C**45**, 231–234.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination and refinement. Univs. of Cambridge, England, and Göttingen, Federal Republic of Germany.

Acta Cryst. (1989). C**45**, 237–239

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

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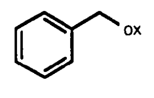
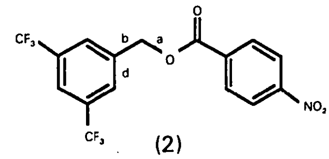
Abstract. $C_{16}H_9F_6NO_4$, $M_r = 393{\cdot}24$, triclinic, $P\bar{1}$, $a = 8{\cdot}500\,(1)$, $b = 9{\cdot}683\,(1)$, $c = 10{\cdot}120\,(1)$ Å, $\alpha = 86{\cdot}96\,(1)$, $\beta = 77{\cdot}19\,(1)$, $\gamma = 82{\cdot}19\,(1)°$, $V = 804{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}62$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}3$ mm^{-1}, $F(000) = 396$, $T = 293$ K, $R = 0{\cdot}060$ 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.



(1*a*) X = CPh$_3$
(1*b*) X = COC$_6$H$_4$NO$_2$



(2)

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 × 0·45 × 0·35 mm, cut from a larger block, was mounted in a glass capillary. A complete sphere of profile-fitted data (Clegg, 1981) to $2\theta_{\max} = 135°$ 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 55–65°.

Of 5617 measured reflections, 2812 were unique ($R_{\mathrm{int}} = 0{\cdot}037$) 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.

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

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