Acta Cryst. (1989). C45, 231–234

Bond Length and Reactivity.* Structures of the Triphenylmethyl and 4-Nitrophenyl Ethers and the 3,5-Dinitrobenzoate Ester of 2,6-Dichlorobenzyl Alcohol

By Peter G. Jones† and Angelika Dölle

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, *D*-3400 *Göttingen,*
Federal Republic of Germany

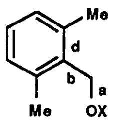
and Anthony J. Kirby and Jane K. Parker

*University Chemical Laboratory, Cambridge CB*2 1*EW, England*

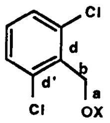
(*Received* 7 *July* 1988; *accepted* 16 *August* 1988)

Abstract. 2,6-Dichlorobenzyl triphenylmethyl ether, $C_{26}H_{20}Cl_2O$, (2*a*), $M_r = 418{\cdot}35$, monoclinic, $P2_1$, $a = 9{\cdot}888\,(2)$, $b = 7{\cdot}468\,(2)$, $c = 14{\cdot}298\,(3)$ Å, $\beta = 90{\cdot}04\,(2)^\circ$, $V = 1055{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}32$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}32$ mm^{-1}, $F(000) = 436$, $T = 293$ K, $R = 0{\cdot}037$ for 3296 unique observed reflections, absolute structure by η [= +0·84 (12)] refinement. 2,6-Dichlorobenzyl 4-nitrophenyl ether, $C_{13}H_9Cl_2NO_3$, (2*b*), $M_r = 298{\cdot}12$, monoclinic, $P2_1/c$, $a = 10{\cdot}311\,(2)$, $b = 11{\cdot}023\,(2)$, $c = 11{\cdot}783\,(2)$ Å, $\beta = 104{\cdot}49\,(6)^\circ$, $V = 1296{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}52$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}50$ mm^{-1}, $F(000) = 608$, $T = 293$ K, $R = 0{\cdot}046$ for 2313 observed reflections. 2,6-Dichlorobenzyl 3,5-dinitrobenzoate, $C_{14}H_8Cl_2N_2O_6$, (2*c*), $M_r = 371{\cdot}13$, monoclinic, $P2_1/n$, $a = 17{\cdot}843\,(3)$, $b = 5{\cdot}056\,(1)$, $c = 18{\cdot}649\,(3)$ Å, $\beta = 114{\cdot}56\,(2)^\circ$, $V = 1530{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}61$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}39$ mm^{-1}, $F(000) = 752$, $T = 293$ K, $R = 0{\cdot}064$ for 1974 observed reflections. In all three derivatives the C—O*X* bond is not far from perpendicular (torsion angle 73±5°) to the ring, and longer for the better 'leaving group': C—O*X* = 1·425 (2), 1·437 (2) and 1·467 (4) Å for (2*a*), (2*b*), (2*c*), respectively.

Introduction. We have reported crystal structures of three derivatives (1) of 2,6-dimethylbenzyl alcohol (Jones *et al.*, 1989), which for steric reasons favour a conformation with the C—O*X* bond close to perpendicular to the plane of the aromatic ring. This paper reports structures for three similar derivatives (2*a*)–(2*c*) of the commercially available 2,6-dichlorobenzyl alcohol, which should have similar properties, though chlorine is a smaller substituent (Taft, 1956) than a methyl group.



(1*a*) X = CPh_3
(1*b*) X = $C_6H_4NO_2$
(1*c*) X = $COC_6H_4NO_2$



(2*a*) X = CPh_3
(2*b*) X = $C_6H_4NO_2$
(2*c*) X = $COC_6H_3(NO_2)_2$

Experimental. The ethers (2*a*) and (2*b*) were prepared as described previously (Jones *et al.*, 1989) for the same derivatives of 2,6-dimethylbenzyl alcohol, and the ester as described for its *p*-nitrobenzoate, using 3,5-dinitrobenzoyl chloride. Crystals were obtained as follows: (2*a*) as colourless prisms, m.p. 413–414 K, by the vapour diffusion method (of hexane into a solution in dichloromethane); (2*b*) as pale yellow blocks, m.p. 402–404 K, by diffusion of hexane into a solution in dichloromethane; and (2*c*) as yellowish prisms, m.p. 437–439 K, by diffusion of hexane into a dichloromethane solution.

Crystals were sealed into glass capillaries; profile-fitted intensities (Clegg, 1981) were registered on a Stoe–Siemens four-circle diffractometer using Mo $K\alpha$ radiation. No corrections for crystal decay (three check reflections) or absorption were necessary. Cell constants were refined from 2θ values of selected strong reflections [48, 84 and 74 reflections for (2*a*)–(2*c*), respectively] in the range 20–25°. Individual details: (2*a*), crystal 0·75 × 0·25 × 0·25 mm, $2\theta_{\max} = 50^\circ$, 4000 reflections including a full set of Friedel opposites, 3697 unique ($R_{\rm int} = 0{\cdot}086$, which is high but involved only reflections at high 2θ, index ranges h −11 to 11, k −8 to 8, l 0 to 16), 3296 observed [$F > 4\sigma(F)$]. (2*b*), crystal 0·7 × 0·4 × 0·3 mm, $2\theta_{\max} = 55^\circ$, 3061 reflections, 2969 unique ($R_{\rm int} = 0{\cdot}037$, index ranges h −13 to 12, k 0 to 14, l 0 to 15), 2313 observed. (2*c*), crystal 0·6 × 0·2 × 0·2 mm, $2\theta_{\max} = 55^\circ$, 4399 reflections, 3512 unique ($R_{\rm int} = 0{\cdot}055$, index ranges h −21 to 20, k 0 to 6, l 0 to 24), 1974 observed.

---

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

† Current address: Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, D-3300 Braunschweig, Federal Republic of Germany.

0108-2701/89/020231-04$03.00 © 1989 International Union of Crystallography

Structures (2*a*) and (2*b*) were solved automatically with the direct-methods routine of the program *SHELX*. (2*c*) resisted attempts at solution until the reflections above $2\theta = 50°$ were omitted. It was originally thought that some erroneous measurements in the shell 50–55° might have caused the problem, but this assumption proved to be incorrect; the same phenomenon was later observed for other structures, and led to an improvement in the direct-methods strategy of the program (Dölle, 1988). Similar developments have been reported by Gilmore & Brown (1988).

The structures were subjected to a full-matrix least-squares refinement on F using a version of *SHELX*76 (Sheldrick, 1976), locally modified by its author. All non-H atoms were anisotropic; H atoms were included using a riding model. Weighting schemes $w^{-1} = \sigma^2(F) + gF^2$ were applied. (2*a*), 261 parameters, $R = 0.037$, $wR = 0.044$, $S = 1.4$, $g = 0.0004$, max. $\Delta/\sigma = 0.002$, max. $\Delta\rho$ within ± 0.2 e Å^{-3}. The absolute structure (Jones, 1984) was determined by an η refinement (Rogers, 1981); $\eta = +0.84$ (12). (2*b*), 172 parameters, $R = 0.046$, $wR = 0.055$, $S = 1.9$, $g = 0.00035$, max. $\Delta/\sigma = 0.005$, max. $\Delta\rho$ within ± 0.2 e Å^{-3}. (2*c*), 217 parameters, $R = 0.064$, $wR = 0.056$, $S = 1.8$, $g = 0.0002$, max. $\Delta/\sigma = 0.03$, max. $\Delta\rho$ within ± 0.3 e Å^{-3}. Atomic scattering factors from *SHELX*76.†

Discussion. Final atom coordinates are given in Table 1, and derived parameters in Table 2. Plots of (2*a*)–(2*c*), showing the atom-numbering schemes, appear in Fig. 1. (2*a*) and (2*b*) are not isostructural with their dimethyl analogues.

The key torsion angle *abd'*, which controls the strength of the ring-π–σ^*_{C-OX} orbital interaction, is 68·2 (5), 78·9 (5) and 73·6 (5)° in (2*a*), (2*b*) and (2*c*), respectively. Though the mean value is a few degrees less than found for the comparable set of derivatives of 2,6-dimethylbenzyl alcohol [69·9 (2), 97·1 (2) and 69·6 (2), 93·7 (2)° (Jones *et al.*, 1989)], all three values are greater than the largest found for a 1-arylethanol derivative (Edwards, Jones & Kirby, 1986), so that the basic objective of a constant conformation appears to be achievable with the 2,6-dichlorobenzyl system also.

The actual C—O*X* bond lengths *a* are similar to those found for the 2,6-dimethylbenzyl alcohol derivatives (Jones, *et al.*, 1989), except that for the triphenylmethyl ether (2*a*), which is significantly shorter [1·425 (2) Å for (2*a*), compared with 1·444 (3) Å]. For (2*a*)–(2*c*) the three C—O*X* bonds increase in length, as expected, with decreasing pK_a of the conjugate acid of

Table 1. *Atomic coordinates* (× 10⁴) *and equivalent isotropic displacement parameters* (Å² × 10³)

	x	*y*	*z*	U_{eq}*
(*a*) Compound (2*a*)				
Cl(1)	2609·3 (7)	9000	6090·6 (5)	78 (1)
Cl(2)	7030·5 (7)	5805 (2)	7566·1 (7)	98 (1)
O(2)	3066 (1)	5386 (2)	7151 (1)	42 (1)
C(1)	3962 (2)	6687 (3)	7536 (1)	45 (1)
C(11)	4839 (2)	7330 (3)	6748 (1)	44 (1)
C(12)	6209 (2)	6971 (4)	6687 (2)	57 (1)
C(13)	6988 (3)	7538 (5)	5920 (3)	77 (1)
C(14)	6380 (3)	8473 (5)	5227 (2)	89 (1)
C(15)	5038 (4)	8896 (4)	5267 (2)	75 (1)
C(16)	4291 (3)	8333 (3)	6028 (2)	53 (1)
C(2)	2340 (2)	4283 (3)	7811 (1)	40 (1)
C(211)	3318 (2)	2863 (3)	8197 (2)	43 (1)
C(212)	4453 (2)	2394 (4)	7666 (2)	54 (1)
C(213)	5335 (3)	1091 (4)	7977 (2)	72 (1)
C(214)	5111 (3)	231 (4)	8800 (2)	78 (1)
C(215)	4001 (3)	641 (4)	9327 (2)	73 (1)
C(216)	3095 (3)	1959 (4)	9030 (2)	57 (1)
C(221)	1225 (2)	3391 (3)	7224 (1)	41 (1)
C(222)	574 (2)	1855 (4)	7536 (2)	58 (1)
C(223)	−471 (3)	1128 (4)	7013 (2)	72 (1)
C(224)	−867 (3)	1875 (5)	6185 (2)	73 (1)
C(225)	−219 (2)	3384 (5)	5871 (2)	65 (1)
C(226)	825 (2)	4126 (4)	6384 (1)	50 (1)
C(231)	1719 (2)	5505 (3)	8563 (1)	40 (1)
C(232)	514 (2)	6393 (3)	8388 (2)	47 (1)
C(233)	−17 (3)	7596 (4)	9025 (2)	59 (1)
C(234)	627 (3)	7896 (4)	9861 (2)	61 (1)
C(235)	1822 (2)	7031 (4)	10046 (2)	58 (1)
C(236)	2368 (2)	5862 (3)	9405 (1)	48 (1)
(*b*) Compound (2*b*)				
O(1)	6673 (1)	2760 (1)	4626 (1)	50 (1)
C(1)	7852 (2)	3368 (2)	5294 (2)	46 (1)
C(11)	8521 (2)	3897 (2)	4421 (2)	43 (1)
C(12)	8074 (2)	4964 (2)	3826 (2)	50 (1)
Cl(12)	6729·2 (6)	5724·1 (6)	4127·3 (6)	76 (1)
C(13)	8666 (3)	5446 (2)	2992 (2)	66 (1)
C(14)	9729 (3)	4856 (3)	2743 (2)	74 (1)
C(15)	10221 (2)	3814 (3)	3316 (2)	68 (1)
C(16)	9620 (2)	3344 (2)	4143 (2)	50 (1)
Cl(16)	10300·3 (6)	2029·8 (6)	4857·5 (6)	74 (1)
N(2)	3139 (2)	404 (2)	6743 (2)	62 (1)
O(2)	3320 (2)	465 (3)	7805 (2)	109 (1)
C(21)	5857 (2)	2207 (2)	5209 (2)	40 (1)
C(22)	4696 (2)	1695 (2)	4505 (2)	47 (1)
C(23)	3807 (2)	1100 (2)	4996 (2)	47 (1)
C(24)	4078 (2)	1029 (2)	6200 (2)	44 (1)
C(25)	5216 (2)	1525 (2)	6915 (2)	47 (1)
C(26)	6120 (2)	2121 (2)	6422 (2)	45 (1)
O(3)	2207 (2)	−138 (2)	6120 (2)	90 (1)
(*c*) Compound (2*c*)				
C(1)	1983 (2)	5755 (8)	3563 (2)	46 (1)
O(1)	1958 (1)	4591 (5)	4188 (1)	52 (1)
O(11)	2392 (1)	7655 (7)	3581 (1)	69 (1)
C(11)	1430 (2)	4454 (7)	2814 (2)	41 (1)
C(12)	1461 (2)	5269 (8)	2120 (2)	42 (1)
C(13)	957 (2)	4083 (7)	1420 (2)	41 (1)
N(13)	1006 (1)	4984 (7)	692 (2)	52 (1)
O(131)	1294 (2)	7166 (7)	694 (2)	73 (1)
O(132)	744 (1)	3509 (6)	125 (1)	67 (1)
C(14)	415 (2)	2102 (8)	1380 (2)	45 (1)
C(15)	386 (2)	1360 (7)	2077 (2)	44 (1)
N(15)	−194 (2)	−748 (7)	2060 (2)	60 (1)
O(151)	−554 (2)	−1904 (7)	1452 (2)	80 (1)
O(152)	−274 (2)	−1151 (8)	2660 (2)	113 (2)
C(16)	882 (2)	2482 (8)	2790 (2)	46 (1)
C(2)	2474 (2)	5742 (9)	4959 (2)	56 (2)
C(21)	2056 (2)	5271 (8)	5490 (2)	44 (1)
C(22)	1361 (2)	6690 (8)	5406 (2)	54 (1)
Cl(22)	954·3 (7)	8975 (3)	4640·4 (7)	86 (1)
C(23)	965 (2)	6383 (10)	5887 (2)	70 (2)
C(24)	1266 (2)	4614 (11)	6490 (3)	79 (2)
C(25)	1949 (3)	3146 (10)	6604 (2)	72 (2)
C(26)	2333 (2)	3458 (9)	6103 (2)	54 (2)
Cl(26)	3176·0 (7)	1458 (3)	6253·2 (7)	86 (1)

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

---

† Lists of H-atom coordinates and U_{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 51332 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Molecular geometry for* (2*a*), (2*b*) *and* (2*c*): *bond lengths* (Å) *and bond angles* (°)

(*a*) Compound (2*a*)

Cl(1)–C(16)	1·738 (3)	Cl(2)–C(12)	1·731 (3)
O(2)–C(1)	1·425 (3)	O(2)–C(2)	1·444 (3)
C(1)–C(11)	1·501 (3)	C(11)–C(12)	1·384 (3)
C(11)–C(16)	1·383 (3)	C(12)–C(13)	1·406 (4)
C(13)–C(14)	1·353 (5)	C(14)–C(15)	1·365 (5)
C(15)–C(16)	1·382 (4)	C(2)–C(211)	1·538 (3)
C(2)–C(221)	1·537 (3)	C(2)–C(231)	1·538 (3)
C(211)–C(212)	1·399 (3)	C(211)–C(216)	1·387 (3)
C(212)–C(213)	1·380 (4)	C(213)–C(214)	1·358 (5)
C(214)–C(215)	1·367 (4)	C(215)–C(216)	1·396 (4)
C(221)–C(222)	1·389 (4)	C(221)–C(226)	1·378 (3)
C(222)–C(223)	1·386 (4)	C(223)–C(224)	1·366 (4)
C(224)–C(225)	1·372 (5)	C(225)–C(226)	1·382 (3)
C(231)–C(232)	1·386 (3)	C(231)–C(236)	1·389 (3)
C(232)–C(233)	1·383 (3)	C(233)–C(234)	1·372 (4)
C(234)–C(235)	1·372 (4)	C(235)–C(236)	1·377 (3)

C(1)–O(2)–C(2)	116·4 (1)	O(2)–C(1)–C(11)	106·7 (2)
C(1)–C(11)–C(12)	123·5 (2)	C(1)–C(11)–C(16)	120·4 (2)
C(12)–C(11)–C(16)	116·2 (2)	Cl(2)–C(12)–C(11)	120·7 (2)
Cl(2)–C(12)–C(13)	117·4 (2)	C(11)–C(12)–C(13)	121·8 (2)
C(12)–C(13)–C(14)	118·9 (3)	C(13)–C(14)–C(15)	121·3 (3)
C(14)–C(15)–C(16)	118·9 (3)	Cl(1)–C(16)–C(11)	110·4 (2)
Cl(1)–C(16)–C(15)	117·7 (2)	C(11)–C(16)–C(15)	122·8 (2)
O(2)–C(2)–C(211)	108·4 (2)	O(2)–C(2)–C(221)	104·3 (1)
C(211)–C(2)–C(221)	110·3 (2)	O(2)–C(2)–C(231)	108·5 (2)
C(211)–C(2)–C(231)	114·2 (2)	C(221)–C(2)–C(231)	110·6 (2)
C(2)–C(211)–C(212)	118·8 (2)	C(2)–C(211)–C(216)	122·9 (2)
C(212)–C(211)–C(216)	118·2 (2)	C(211)–C(212)–C(213)	120·6 (2)
C(212)–C(213)–C(214)	120·6 (3)	C(213)–C(214)–C(215)	120·2 (3)
C(214)–C(215)–C(216)	120·3 (3)	C(211)–C(216)–C(215)	120·1 (2)
C(2)–C(221)–C(222)	121·0 (2)	C(2)–C(221)–C(226)	120·6 (2)
C(222)–C(221)–C(226)	118·4 (2)	C(221)–C(222)–C(223)	119·7 (2)
C(222)–C(223)–C(224)	121·4 (3)	C(223)–C(224)–C(225)	119·0 (3)
C(224)–C(225)–C(226)	120·3 (2)	C(221)–C(226)–C(225)	121·1 (2)
C(2)–C(231)–C(232)	120·1 (2)	C(2)–C(231)–C(236)	122·4 (2)
C(232)–C(231)–C(236)	117·4 (2)	C(231)–C(232)–C(233)	121·2 (2)
C(232)–C(233)–C(234)	120·2 (2)	C(233)–C(234)–C(235)	119·4 (2)
C(234)–C(235)–C(236)	120·5 (2)	C(231)–C(236)–C(235)	121·2 (2)

(*b*) Compound (2*b*)

O(1)–C(1)	1·437 (2)	O(1)–C(21)	1·358 (2)
C(1)–C(11)	1·494 (3)	C(11)–C(12)	1·387 (3)
C(11)–C(16)	1·396 (3)	C(12)–Cl(12)	1·732 (2)
C(12)–C(13)	1·386 (3)	C(13)–C(14)	1·369 (4)
C(14)–C(15)	1·365 (4)	C(15)–C(16)	1·380 (4)
C(16)–Cl(16)	1·733 (2)	N(2)–O(2)	1·220 (3)
N(2)–C(24)	1·460 (3)	N(2)–O(3)	1·211 (3)
C(21)–C(22)	1·393 (2)	C(21)–C(26)	1·389 (3)
C(22)–C(23)	1·369 (3)	C(23)–C(24)	1·378 (3)
C(24)–C(25)	1·374 (2)	C(25)–C(26)	1·382 (3)

C(1)–O(1)–C(21)	118·6 (1)	O(1)–C(1)–C(11)	106·1 (1)
C(1)–C(11)–C(12)	121·8 (2)	C(1)–C(11)–C(16)	122·2 (2)
C(12)–C(11)–C(16)	116·0 (2)	C(11)–C(12)–Cl(12)	119·2 (2)
C(11)–C(12)–C(13)	122·3 (2)	Cl(12)–C(12)–C(13)	118·5 (2)
C(12)–C(13)–C(14)	119·2 (2)	C(13)–C(14)–C(15)	120·8 (3)
C(14)–C(15)–C(16)	119·3 (2)	C(11)–C(16)–C(15)	122·4 (2)
C(11)–C(16)–Cl(16)	120·3 (2)	C(15)–C(16)–Cl(16)	117·3 (2)
O(2)–N(2)–C(24)	118·4 (2)	O(2)–N(2)–O(3)	122·9 (2)
C(24)–N(2)–O(3)	118·7 (2)	O(1)–C(21)–C(22)	115·4 (2)
O(1)–C(21)–C(26)	124·4 (2)	C(22)–C(21)–C(26)	120·2 (2)
C(21)–C(22)–C(23)	120·6 (2)	C(22)–C(23)–C(24)	118·5 (2)
N(2)–C(24)–C(23)	119·4 (2)	N(2)–C(24)–C(25)	118·5 (2)
C(23)–C(24)–C(25)	122·1 (2)	C(24)–C(25)–C(26)	119·5 (2)
C(21)–C(26)–C(25)	119·1 (2)		

(*c*) Compound (2*c*)

C(1)–O(1)	1·323 (5)	C(1)–O(11)	1·198 (5)
C(1)–C(11)	1·488 (4)	O(1)–C(2)	1·467 (4)
C(11)–C(12)	1·381 (5)	C(11)–C(16)	1·384 (5)
C(12)–C(13)	1·377 (4)	C(13)–N(13)	1·470 (5)
C(13)–C(14)	1·373 (5)	N(13)–O(131)	1·216 (5)
N(13)–O(132)	1·218 (4)	C(14)–C(15)	1·374 (5)
C(15)–N(15)	1·477 (5)	C(15)–C(16)	1·377 (4)
N(15)–O(151)	1·197 (4)	N(15)–O(152)	1·203 (5)
C(2)–C(21)	1·486 (6)	C(21)–C(22)	1·383 (5)
C(21)–C(26)	1·387 (5)	C(22)–Cl(22)	1·743 (4)
C(22)–C(23)	1·362 (7)	C(23)–C(24)	1·361 (7)
C(24)–C(25)	1·366 (7)	C(25)–C(26)	1·378 (7)
C(26)–Cl(26)	1·736 (4)		

Table 2 (*cont*.)

O(11)–C(1)–O(1)	125·2 (3)	C(11)–C(1)–O(1)	112·2 (3)
C(11)–C(1)–O(11)	122·6 (3)	C(2)–O(1)–C(1)	116·7 (3)
C(12)–C(11)–C(1)	118·6 (3)	C(16)–C(11)–C(1)	122·2 (3)
C(16)–C(11)–C(12)	119·2 (3)	C(13)–C(12)–C(11)	119·5 (3)
N(13)–C(13)–C(12)	118·3 (3)	C(14)–C(13)–C(12)	122·6 (3)
C(14)–C(13)–N(13)	119·1 (3)	O(131)–N(13)–C(13)	117·7 (3)
O(132)–N(13)–C(13)	117·7 (3)	O(132)–N(13)–O(131)	124·6 (3)
C(15)–C(14)–C(13)	116·7 (3)	N(15)–C(15)–C(14)	118·5 (3)
C(16)–C(15)–C(14)	122·7 (3)	C(16)–C(15)–N(15)	118·8 (3)
O(151)–N(15)–C(15)	117·9 (3)	O(152)–N(15)–C(15)	117·1 (3)
O(152)–N(15)–O(151)	125·0 (4)	C(15)–C(16)–C(11)	119·3 (4)
C(21)–C(2)–O(1)	107·8 (3)	C(22)–C(21)–C(2)	121·0 (3)
C(26)–C(21)–C(2)	123·3 (3)	C(26)–C(21)–C(22)	115·6 (4)
Cl(22)–C(22)–C(21)	119·0 (3)	C(23)–C(22)–C(21)	123·5 (4)
C(23)–C(22)–Cl(22)	117·5 (3)	C(24)–C(23)–C(22)	119·0 (4)
C(25)–C(24)–C(23)	120·4 (5)	C(26)–C(25)–C(24)	119·7 (4)
C(25)–C(26)–C(21)	121·8 (4)	Cl(26)–C(26)–C(21)	120·4 (3)
Cl(26)–C(26)–C(25)	117·7 (3)		

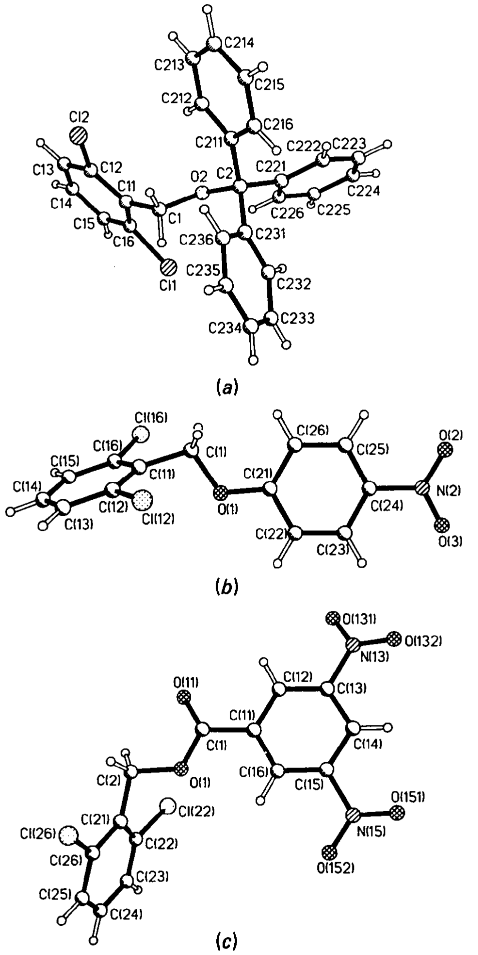


Fig. 1. (*a*) Molecular structure of (2*a*), showing the atom-numbering scheme. (*b*) Molecular structure of (2*b*), showing the atom-numbering scheme. (*c*) Molecular structure of (2*c*), showing the atom-numbering scheme.

the leaving group HO*X*; but the three points do not define a good straight line (see Edwards *et al.*, 1986): linear regression gives a correlation coefficient, $r = 0{\cdot}911$ for the three points. However, there are clearly not enough data to permit general conclusions at this stage.

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.

Acta Cryst. (1989). C**45**, 234–237

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

By Peter G. Jones† and Angelika Dölle

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

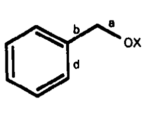
and Anthony J. Kirby and Jane K. Parker

University Chemical Laboratory, Cambridge CB2 1EW, England

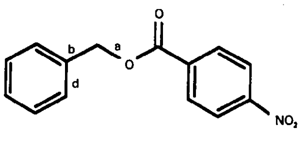
(*Received 7 July* 1988; *accepted* 16 *August* 1988)

Abstract. Benzyl triphenylmethyl ether (1), $C_{26}H_{22}O$, $M_r = 350{\cdot}46$, monoclinic, $P2_1/n$, $a = 9{\cdot}539\,(2)$, $b = 10{\cdot}681\,(2)$, $c = 19{\cdot}680\,(3)$ Å, $\beta = 101{\cdot}29\,(2)^\circ$, $V = 1966{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}18$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}07$ mm^{-1}, $F(000) = 744$, $T = 293$ K, $R = 0{\cdot}053$ for 3561 unique observed reflections. Benzyl 4-nitrobenzoate (2), $C_{14}H_{11}NO_4$, $M_r = 257{\cdot}25$, monoclinic, $P2_1/n$, $a = 6{\cdot}180\,(2)$, $b = 7{\cdot}717\,(2)$, $c = 26{\cdot}277\,(6)$ Å, $\beta = 93{\cdot}02\,(2)^\circ$, $V = 1251{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}37$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}09$ mm^{-1}, $F(000) = 536$, $T = 293$ K, $R = 0{\cdot}053$ 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 $ArCH_2OX$ 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)

---

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

[†] Current address: Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, D-3300 Braunschweig, Federal Republic of Germany.

0108-2701/89/020234-04$03.00

© 1989 International Union of Crystallography