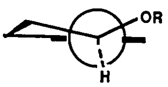
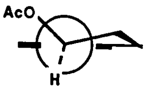
are different, and both differ also from that of the triphenylmethyl ethers described in the previous paper (Jones *et al.*, 1989). Since the two ethers have almost identical conformations, we compare the two ester structures with that of the unsubstituted ether (1).

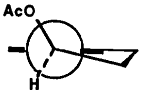
Evidently tying back the benzylic substituent group in a five-membered ring fails to produce the desired effect of fixing the conformation about the ring—C_α bond when different leaving groups are involved. The three structures have torsion angles *abd'* of 75·2 (3), 54·7 (4) (ester) and −36·2 (3)° (ether), even though the puckering of the ring changes rather little [torsion angles *cbd* of 14·3 (3), −8·3 (3) and 19·7 (2)°, respectively]. The trend observed for simple 1-arylethanol derivatives, of an increase in the torsion angle *abd'* on going from ether to ester, is apparent in these 1-indanol derivatives also: as a result it is the α-H, rather than the $OCPh_3$ group, which lies close to perpendicular to the ring in the ether (1). This torsion angle is greater for molecule *A*, and greatest for molecule *B* of (2).



(1)



(2*A*)



(2*B*)

As is to be expected, in view of our previous work, the C—O*X* bond lengths *a* also increase in this series from (1) to (2), because the ester provides a better (less basic) leaving group O*X*, and from molecule *A* to *B* of (2), because the dihedral angle *abd'* increases. The *differences* in bond length *a* are exactly as predicted by the correlations we derived for the 1-arylethanol derivatives (Edwards *et al.*, 1986). From the correlation quoted in this paper we can calculate values of 1·470, 1·479 and 1·443 Å for the corresponding 1-arylethyl ester and ether, respectively, with ring—C—O*X* torsion angles as found for (2*A*), (2*B*) and (1). The observed values are 1·462 (3), 1·470 (3) and 1·432 (3) Å. These absolute magnitudes are consistently shorter than predicted for the open-chain system, by 0·009±0·001 Å. This is a small difference, but consistent with the lower reactivity of five-membered ring *vs* open-chain compounds, which is accounted for by the geometrical restriction at the substituted centre. There is a striking difference between the open-chain 1-arylethyl derivatives, where the bond angle *bc* opens up from normal tetrahedral values (109–110°) in alkyl ethers to 113–115·8° in the esters (Edwards *et al.*, 1986), and the 1-indanol derivatives (1) and (2), where the increase is from 102·4 to 104·9°. This angle must open to near 120° in the transition state for heterolytic cleavage of the C—O*X* bond.

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Bond Length and Reactivity.* Structures of the Triphenylmethyl and 4-Nitrophenyl Ethers and the 4-Nitrobenzoate Ester of 2,6-Dimethylbenzyl Alcohol

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Abstract. 2,6-Dimethylbenzyl triphenylmethyl ether (3*a*), $C_{28}H_{26}O$, $M_r = 378\cdot5$, orthorhombic, $Pca2_1$, $a = 28\cdot271$ (2), $b = 9\cdot981$ (1), $c = 7\cdot668$ (1) Å, $V = 2163\cdot5$ Å^3, $Z = 4$, $D_x = 1\cdot16$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot5418$ Å, $\mu = 0\cdot46$ mm^{-1}, $F(000) = 808$, $T = 293$ K, $R = 0\cdot056$ for 2768 unique observed reflections. 2,6-Dimethylbenzyl 4-nitrophenyl ether (3*b*), $C_{15}H_{15}NO_3$, $M_r = 257\cdot3$, monoclinic, $P2_1/c$, $a = 8\cdot691$ (1), $b = 11\cdot506$ (1), $c = 13\cdot700$ (2) Å, $\beta = 94\cdot90$ (1)°, V

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

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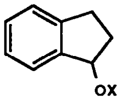
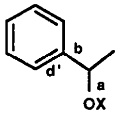
$= 1365{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}25$ Mg m^{-3}, λ(Cu $K\alpha$) = $1{\cdot}5418$ Å, $\mu = 0{\cdot}68$ mm^{-1}, $F(000) = 544$, $T = 293$ K, $R = 0{\cdot}057$ for 1841 observed reflections. 2,6-Dimethylbenzyl 4-nitrobenzoate (3*c*), $C_{16}H_{15}NO_4$, $M_r = 285{\cdot}3$, triclinic, $P\bar{1}$, $a = 8{\cdot}208$ (1), $b = 13{\cdot}496$ (1), $c = 14{\cdot}215$ (2) Å, $\alpha = 105{\cdot}67$ (1), $\beta = 103{\cdot}13$ (1), $\gamma = 93{\cdot}99$ (1)°, $V = 1462{\cdot}0$ Å^3, $Z = 4$ (two independent molecules), $D_x = 1{\cdot}30$ Mg m^{-3}, λ(Cu $K\alpha$) = $1{\cdot}5418$ Å, $\mu = 0{\cdot}74$ mm^{-1}, $T = 293$ K, $R = 0{\cdot}048$ for 3483 observed reflections. The three derivatives crystallize in similar conformations over the 2,6-dimethylbenzyl structural subunit, with the C—O*X* bond close to perpendicular to the aromatic ring [torsion angles 69·9, −112·7; 97·1, −83·7; 69·6, −114·7 and 93·7, −85·3 (2)° for (3*a*), (3*b*) and the two independent molecules of (3*c*), respectively]. The corresponding CH_2—O*X* bond lengths are 1·444 (3), 1·441 (2), 1·458 (2) and 1·467 (2) Å.

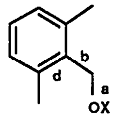
Introduction. As part of our wider investigation of bond length–reactivity correlations (Jones & Kirby, 1984; Edwards, Jones & Kirby, 1986) we are seeking benzylic systems with a fixed conformation about the ring—C_α bond. We found that the 1-indanol system (1) is too conformationally flexible for this purpose (Kirby, Parker & Raithby, 1989). The problem is that in a 1-arylethanol derivative (2) the conformation with the C—Me bond perpendicular to the aromatic ring is preferred in most cases, but making OX^- a better leaving group increasingly favours the conformation with the C—O*X* bond perpendicular. A solution would be to use a system in which the C—O*X* bond prefers this conformation even for aliphatic ethers (X = alkyl). A simple system which appears promising is 2,6-dimethylbenzyl alcohol [(3), X = H], in which non-bonded repulsions involving the two *ortho*-methyl groups should ensure that the C—O*X* bond lies close to the perpendicular conformation. We have prepared three representative derivatives, the triphenylmethyl and 4-nitrophenyl ethers, and the 4-nitrobenzoate ester, (3*a*)–(3*c*), and report their crystal structures.



(1)



(2)



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

Experimental. 2,6-Dimethylbromobenzene was carboxylated *via* a Grignard reagent with EtO_2CCl, and the ester reduced with lithium aluminium hydride to 2,6-dimethylbenzyl alcohol. This was converted to the lithium salt by reaction with *n*-butyllithium and arylated with 4-nitrofluorobenzene, or acylated with 4-nitrobenzoyl chloride, to give ether (3*b*) and ester (3*c*), respectively. The triphenylmethyl ether (3*a*) was prepared by alkylating the alcohol with triphenylmethyl chloride in dichloromethane in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine, as described for other triphenylmethyl ethers (Jones, Schmidt-Bäse, Kirby & Parker, 1989). Crystallization of (3*a*): liquid diffusion of petrol into a solution in dichloromethane failed, but slow evaporation of the resulting solution gave colourless needles, m.p. 402–403 K; of (3*b*): diffusion of petrol into a solution in dichloromethane gave yellow prisms, m.p. 414–416 K; of (3*c*): diffusion of 40–60° petrol vapour into a dichloromethane solution gave colourless blocks, m.p. 367–367·5 K. Crystals of (3*c*) were also obtained as colourless prisms, space group $I222$ or $I2_12_12_1$, approximate cell constants a, b, c = 4·3, 22·6, 30·9 Å, $Z = 8$, but no crystal of measurable quality was found.

Intensity measurements were performed on a Stoe–Siemens four-circle diffractometer in profile-fitting mode (Clegg, 1981) using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). (3*a*): crystal 0·7 × 0·2 × 0·1 mm, 3601 reflections, 2768 with $F > 4\sigma(F)$ used for all calculations (program system *SHELX*76, modified locally by its author, Professor G. M. Sheldrick). Index ranges after merging; h 0 to 33, k 0 to 11, l −8 to 8. No crystal decay (three check reflections), no correction for absorption or extinction. Cell constants refined from 2θ values of 52 reflections in the range 60–70°. (3*b*): as for (3*a*) except: crystal 0·6 × 0·3 × 0·2 mm, 4506 reflections (one complete hemisphere), 2276 unique ($R_{\rm int} = 0{\cdot}030$), 1841 observed, index ranges h −10 to 10, k 0 to 13, l 0 to 16. Cell constants refined from 56 2θ values. No decay, no absorption correction. (3*c*): as for (3*a*) except: crystal size 0·55 × 0·4 × 0·3 mm, 4343 unique reflections (one hemisphere), 3843 observed, index ranges h −9 to 9, k −15 to 15, l 0 to 16.

Structure solution and refinement: routine direct methods followed by anisotropic full-matrix least-squares refinement on F. H atoms included using a riding model. (3*a*): $R = 0{\cdot}056$, $wR = 0{\cdot}060$, weighting scheme $w^{-1} = \sigma^2(F) + gF^2$, with $g = 0{\cdot}0005$, 261 parameters, $S = 1{\cdot}5$, max. $\Delta/\sigma = 0{\cdot}003$, max. $\Delta\rho$ within $\pm 0{\cdot}25$ e Å^{-3}. (3*b*): $R = 0{\cdot}057$, $wR = 0{\cdot}067$, $g = 0{\cdot}0002$, 185 parameters, $S = 2{\cdot}7$, max. $\Delta/\sigma = 0{\cdot}7$ for disordered methyl group (see below), otherwise $<0{\cdot}01$, max. $\Delta\rho$ within $\pm 0{\cdot}2$ e Å^{-3}. (3*c*): $R = 0{\cdot}048$, $wR = 0{\cdot}059$, $g = 0{\cdot}0002$, 404 parameters, $S = 2{\cdot}4$, max. $\Delta/\sigma = 0{\cdot}18$ for disordered methyl group (see below), otherwise 0·003, max. $\Delta\rho$ within $\pm 0{\cdot}015$ e Å^{-3}. Atomic scattering factors from *SHELX*76.

Special features of refinement: (3*a*): absolute structure was not determined. (3*b*): the methyl groups were disordered, presumably because of their low torsional energy barrier, and were refined as six half-occupied H atoms in a regular hexagon. The lack of convergence of the associated parameters suggests that this model may be an over-simplification. An extinction coefficient correction of the form $F_{\rm corr} = F_c/(1 + xF^2/\sin 2\theta)^{0.25}$ was

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

	x	y	z	U_{eq}*
(*a*) Compound (3*a*)				
O(1)	1419·1 (6)	3103 (2)	4000	49 (1)
C(1)	1216 (1)	4029 (3)	2762 (5)	55 (1)
C(2)	1086 (1)	2383 (3)	5058 (4)	44 (1)
C(11)	1609 (1)	4895 (3)	2081 (4)	49 (1)
C(12)	1950 (1)	4304 (3)	977 (4)	61 (1)
C(13)	2315 (1)	5096 (4)	318 (5)	86 (2)
C(14)	2331 (1)	6444 (5)	733 (5)	92 (2)
C(15)	1996 (1)	7017 (4)	1750 (6)	83 (2)
C(16)	1630 (1)	6250 (3)	2450 (5)	59 (1)
C(17)	1922 (2)	2846 (4)	476 (6)	85 (2)
C(18)	1270 (2)	6944 (3)	3589 (7)	95 (2)
C(21)	715 (1)	1743 (3)	3857 (4)	43 (1)
C(22)	283 (1)	2360 (3)	3506 (5)	56 (1)
C(23)	−26 (1)	1811 (3)	2285 (5)	66 (1)
C(24)	90 (1)	667 (4)	1393 (6)	72 (1)
C(25)	517 (1)	59 (4)	1703 (5)	70 (1)
C(26)	826 (1)	603 (3)	2925 (5)	57 (1)
C(31)	1382 (1)	1294 (3)	5985 (5)	47 (1)
C(32)	1855 (1)	1098 (3)	5578 (6)	68 (1)
C(33)	2107 (1)	89 (4)	6406 (7)	84 (1)
C(34)	1905 (1)	−728 (4)	7598 (6)	72 (1)
C(35)	1439 (1)	−531 (4)	8001 (6)	72 (1)
C(36)	1181 (1)	463 (3)	7221 (6)	64 (1)
C(41)	892 (1)	3335 (3)	6477 (5)	52 (1)
C(42)	1167 (1)	4403 (3)	6993 (5)	64 (1)
C(43)	1021 (2)	5266 (4)	8309 (6)	85 (2)
C(44)	607 (2)	5057 (4)	9121 (7)	91 (2)
C(45)	322 (2)	3991 (5)	8673 (7)	87 (2)
C(46)	463 (1)	3109 (4)	7333 (6)	66 (1)
(*b*) Compound (3*b*)				
C(1)	6135 (2)	7878 (2)	4644 (2)	77 (1)
C(11)	4674 (2)	8342 (2)	4988 (2)	70 (1)
C(12)	4645 (2)	8765 (2)	5940 (2)	78 (1)
C(13)	3269 (3)	9215 (2)	6222 (2)	92 (1)
C(14)	1968 (3)	9250 (2)	5588 (2)	103 (1)
C(15)	2007 (3)	8826 (2)	4668 (2)	101 (1)
C(16)	3342 (3)	8360 (2)	4344 (2)	83 (1)
C(17)	6036 (3)	8729 (3)	6665 (2)	108 (1)
C(18)	3321 (4)	7891 (3)	3330 (2)	124 (1)
C(21)	7256 (2)	6001 (2)	4378 (1)	62 (1)
C(22)	8445 (2)	6462 (2)	3899 (2)	76 (1)
C(23)	9507 (2)	5725 (2)	3533 (2)	79 (1)
C(24)	9383 (2)	4551 (2)	3661 (1)	67 (1)
C(25)	8214 (2)	4085 (2)	4139 (2)	74 (1)
C(26)	7144 (2)	4809 (2)	4493 (2)	74 (1)
N(1)	10505 (2)	3775 (2)	3265 (2)	90 (1)
O(1)	6114 (2)	6632 (1)	4746 (1)	77 (1)
O(2)	11500 (2)	4180 (2)	2814 (2)	161 (1)
O(3)	10410 (2)	2743 (2)	3413 (2)	124 (1)
(*c*) Compound (3*c*)				
C(1)	−424 (3)	1438 (2)	1600 (2)	79 (1)
C(11)	−145 (3)	1439 (2)	595 (2)	61 (1)
C(12)	1487 (3)	1462 (2)	464 (2)	63 (1)
C(13)	1708 (3)	1381 (2)	−492 (2)	69 (1)
C(14)	364 (3)	1284 (2)	−1295 (2)	71 (1)
C(15)	−1228 (3)	1262 (2)	−1168 (2)	75 (1)
C(16)	−1519 (3)	1346 (2)	−227 (2)	69 (1)
C(17)	3003 (3)	1567 (2)	1317 (2)	95 (1)
C(18)	−3307 (4)	1321 (3)	−130 (3)	113 (2)
N(1)	3588 (3)	6182 (2)	6348 (2)	92 (1)
O(1)	266 (2)	2446 (1)	2340 (1)	71 (1)
C(2)	58 (3)	2526 (2)	3258 (2)	64 (1)
C(21)	995 (3)	3498 (2)	4030 (2)	59 (1)
C(22)	1938 (3)	4249 (2)	3806 (2)	70 (1)
C(23)	2800 (3)	5128 (2)	4565 (2)	77 (1)
C(24)	2678 (3)	5238 (2)	5529 (2)	70 (1)
C(25)	1767 (3)	4514 (2)	5776 (2)	77 (1)
C(26)	923 (3)	3634 (2)	5023 (2)	71 (1)
O(2)	4475 (3)	6792 (2)	6125 (2)	136 (1)
O(21)	−763 (2)	1869 (1)	3449 (1)	89 (1)
O(3)	3345 (3)	6302 (2)	7186 (2)	123 (1)
C(1′)	4538 (3)	7867 (2)	3621 (2)	73 (1)
C(11′)	4146 (3)	8945 (2)	3686 (2)	59 (1)
C(12′)	2688 (3)	9256 (2)	3967 (2)	63 (1)
C(13′)	2357 (3)	10254 (2)	4011 (2)	71 (1)
C(14′)	3429 (3)	10934 (2)	3794 (2)	74 (1)
C(15′)	4844 (3)	10632 (2)	3513 (2)	68 (1)
C(16′)	5226 (3)	9636 (2)	3453 (2)	62 (1)
C(17′)	1479 (3)	8539 (2)	4214 (2)	92 (1)
C(18′)	6786 (3)	9331 (2)	3130 (2)	90 (1)
N(1′)	1392 (3)	3951 (2)	−1792 (2)	94 (1)
O(1′)	3837 (2)	7234 (1)	2568 (1)	71 (1)
C(2′)	3997 (3)	6228 (2)	2367 (2)	66 (1)
C(21′)	3302 (3)	5656 (2)	1277 (2)	65 (1)
C(22′)	2344 (3)	6096 (2)	612 (2)	76 (1)
C(23′)	1705 (3)	5543 (2)	−395 (2)	81 (1)
C(24′)	2071 (3)	4552 (2)	−716 (2)	75 (1)
C(25′)	3040 (4)	4099 (2)	−76 (2)	88 (1)
C(26′)	3646 (3)	4654 (2)	936 (2)	81 (1)
O(21′)	4626 (3)	5829 (1)	2992 (1)	89 (1)
O(2′)	181 (3)	4233 (2)	−2288 (2)	123 (1)
O(3′)	2100 (3)	3221 (2)	−2126 (2)	130 (1)

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

applied, where x refined to 4·3 (4) × 10^{-5}. (3*c*): two molecules in the asymmetric unit: the methyl groups were disordered as for (3*b*), but the hexagon model converged better. A similar extinction correction gave $x = 4{\cdot}2\ (3) \times 10^{-5}$.

Discussion. Final atom coordinates are given in Table 1 and derived parameters in Table 2.* Plots for (3*a*)–(3*c*), showing the atom-numbering schemes, appear in Fig. 1. The packing diagram for (3*c*) (Fig. 2) shows how the two independent molecules pack in independent layers parallel to 011.

The two molecules of (3*c*) differ mainly in the torsion angles O(1)—C(2)—C(21)—C(22), 1·8 and −10·9°, and O(1)—C(1)—C(11)—C(12), 69·6 (5) and −93·7 (5)°, respectively, *i.e.* in the orientation of the rings. This is apparent from Figs. 1(*c*), 1(*d*) and 2. But within the 2,6-dimethylbenzyloxy structural unit the three compounds crystallize in similar conformations, close to the desired perpendicular arrangement of ring and C—O*X* bond, and close to antiperiplanar about the C—O*X* bond. In terms of the key torsion angle θ (=$|90 - |abd||$) between the π and $\sigma^*_{\mathrm{C-O}X}$ orbitals the observed values are 20·1 (4), 6·3 (4), 20·4 (4) and 3·7 (4)° for (3*a*), (3*b*) and the two independent molecules of (3*c*), respectively. These correspond to values of $\cos^2\theta$ between 0·878 and 0·996. For 1-arylethanol derivatives, where the influence of conformation on the C—O*X* bond length was quantified [coefficient $-1{\cdot}33 \times 10^{-2}\cos^2\theta$ (Edwards *et al.*, 1986)], this corresponds to a difference of 0·002 Å, less than one standard

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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 51331 (45 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* (3*a*), (3*b*) *and* (3*c*): *bond lengths* (Å) *and bond angles* (°)

(*a*) Compound (3*a*)

O(1)–C(1)	1·444 (3)	O(1)–C(2)	1·435 (3)
C(1)–C(11)	1·502 (4)	C(2)–C(21)	1·534 (4)
C(2)–C(31)	1·545 (4)	C(2)–C(41)	1·545 (4)
C(11)–C(12)	1·412 (4)	C(11)–C(16)	1·383 (4)
C(12)–C(13)	1·394 (5)	C(12)–C(17)	1·507 (5)
C(13)–C(14)	1·384 (6)	C(14)–C(15)	1·354 (6)
C(15)–C(16)	1·395 (5)	C(16)–C(18)	1·509 (6)
C(21)–C(22)	1·396 (4)	C(21)–C(26)	1·380 (4)
C(22)–C(23)	1·392 (5)	C(23)–C(24)	1·370 (5)
C(24)–C(25)	1·372 (5)	C(25)–C(26)	1·392 (5)
C(31)–C(32)	1·388 (4)	C(31)–C(36)	1·381 (5)
C(32)–C(33)	1·387 (5)	C(33)–C(34)	1·352 (6)
C(34)–C(35)	1·366 (5)	C(35)–C(36)	1·369 (5)
C(41)–C(42)	1·376 (5)	C(41)–C(46)	1·397 (5)
C(42)–C(43)	1·388 (6)	C(43)–C(44)	1·342 (7)
C(44)–C(45)	1·380 (7)	C(45)–C(46)	1·410 (7)

C(2)–O(1)–C(1)	115·6 (2)	C(11)–C(1)–O(1)	107·7 (2)
C(21)–C(2)–O(1)	108·5 (2)	C(31)–C(2)–O(1)	104·9 (2)
C(31)–C(2)–C(21)	110·7 (2)	C(41)–C(2)–O(1)	108·8 (2)
C(41)–C(2)–C(21)	115·9 (2)	C(41)–C(2)–C(31)	107·5 (3)
C(12)–C(11)–C(1)	118·2 (3)	C(16)–C(11)–C(1)	121·5 (3)
C(16)–C(11)–C(12)	120·2 (3)	C(13)–C(12)–C(11)	119·0 (3)
C(17)–C(12)–C(11)	121·4 (3)	C(17)–C(12)–C(13)	119·6 (3)
C(14)–C(13)–C(12)	119·5 (3)	C(15)–C(14)–C(13)	121·4 (4)
C(16)–C(15)–C(14)	120·6 (4)	C(15)–C(16)–C(11)	119·3 (3)
C(18)–C(16)–C(11)	122·6 (3)	C(18)–C(16)–C(15)	118·1 (3)
C(22)–C(21)–C(2)	122·0 (3)	C(26)–C(21)–C(2)	119·9 (2)
C(26)–C(21)–C(22)	117·6 (3)	C(23)–C(22)–C(21)	120·3 (3)
C(24)–C(23)–C(22)	120·9 (3)	C(25)–C(24)–C(23)	119·5 (4)
C(26)–C(25)–C(24)	119·8 (3)	C(25)–C(26)–C(21)	121·8 (3)
C(32)–C(31)–C(2)	121·2 (3)	C(36)–C(31)–C(2)	121·0 (3)
C(36)–C(31)–C(32)	117·8 (3)	C(33)–C(32)–C(31)	119·6 (3)
C(34)–C(33)–C(32)	122·0 (3)	C(35)–C(34)–C(33)	118·3 (4)
C(36)–C(35)–C(34)	121·3 (4)	C(35)–C(36)–C(31)	121·0 (3)
C(42)–C(41)–C(2)	118·6 (3)	C(46)–C(41)–C(2)	122·6 (3)
C(46)–C(41)–C(42)	118·6 (3)	C(43)–C(42)–C(41)	121·5 (4)
C(44)–C(43)–C(42)	119·9 (4)	C(45)–C(44)–C(43)	121·0 (5)
C(46)–C(45)–C(44)	119·7 (4)	C(45)–C(46)–C(41)	119·2 (4)

(*b*) Compound (3*b*)

C(1)–C(11)	1·491 (3)	C(1)–O(1)	1·441 (2)
C(11)–C(12)	1·394 (3)	C(11)–C(16)	1·394 (3)
C(12)–C(13)	1·389 (3)	C(12)–C(17)	1·498 (3)
C(13)–C(14)	1·367 (3)	C(14)–C(15)	1·354 (4)
C(15)–C(16)	1·385 (4)	C(16)–C(18)	1·489 (4)
C(21)–C(22)	1·377 (3)	C(21)–C(26)	1·385 (3)
C(21)–O(1)	1·361 (2)	C(22)–C(23)	1·378 (3)
C(23)–C(24)	1·368 (3)	C(24)–C(25)	1·365 (3)
C(24)–N(1)	1·460 (3)	C(25)–C(26)	1·369 (3)
N(1)–O(2)	1·200 (3)	N(1)–O(3)	1·208 (3)

O(1)–C(1)–C(11)	107·9 (2)	C(12)–C(11)–C(1)	120·3 (2)
C(16)–C(11)–C(1)	119·3 (2)	C(16)–C(11)–C(12)	120·4 (2)
C(13)–C(12)–C(11)	118·4 (2)	C(17)–C(12)–C(11)	122·2 (2)
C(17)–C(12)–C(13)	119·4 (2)	C(14)–C(13)–C(12)	121·3 (2)
C(15)–C(14)–C(13)	119·8 (2)	C(16)–C(15)–C(14)	121·7 (2)
C(15)–C(16)–C(11)	118·4 (2)	C(18)–C(16)–C(11)	121·9 (2)
C(18)–C(16)–C(15)	119·7 (2)	C(26)–C(21)–C(22)	119·9 (2)
O(1)–C(21)–C(22)	124·9 (2)	O(1)–C(21)–C(26)	115·1 (2)
C(23)–C(22)–C(21)	119·3 (2)	C(24)–C(23)–C(22)	119·9 (2)
C(25)–C(24)–C(23)	121·3 (2)	N(1)–C(24)–C(23)	119·6 (2)
N(1)–C(24)–C(25)	119·1 (2)	C(26)–C(25)–C(24)	119·2 (2)
C(25)–C(26)–C(21)	120·4 (2)	O(2)–N(1)–C(24)	119·1 (2)
O(3)–N(1)–C(24)	118·8 (2)	O(3)–N(1)–O(2)	122·1 (2)
C(21)–O(1)–C(1)	118·6 (2)		

(*c*) Compound (3*c*)

C(1)–C(11)	1·498 (4)	C(1′)–C(11′)	1·495 (3)
C(1)–O(1)	1·458 (2)	C(1′)–O(1′)	1·467 (2)
C(11)–C(12)	1·393 (3)	C(11′)–C(12′)	1·401 (3)
C(11)–C(16)	1·398 (3)	C(11′)–C(16′)	1·396 (3)
C(12)–C(13)	1·388 (4)	C(12′)–C(13′)	1·381 (4)
C(12)–C(17)	1·496 (3)	C(12′)–C(17′)	1·501 (4)
C(13)–C(14)	1·365 (3)	C(13′)–C(14′)	1·368 (4)
C(14)–C(15)	1·358 (4)	C(14′)–C(15′)	1·365 (4)
C(15)–C(16)	1·388 (4)	C(15′)–C(16′)	1·386 (3)
C(16)–C(18)	1·505 (4)	C(16′)–C(18′)	1·502 (4)
N(1)–C(24)	1·485 (3)	N(1′)–C(24′)	1·479 (3)
N(1)–O(2)	1·212 (4)	N(1′)–O(2′)	1·228 (3)
N(1)–O(3)	1·222 (4)	N(1′)–O(3′)	1·219 (3)
O(1)–C(2)	1·331 (3)	O(1′)–C(2′)	1·332 (3)
C(2)–C(21)	1·488 (2)	C(2′)–C(21′)	1·487 (3)
C(2)–O(21)	1·201 (3)	C(2′)–O(21′)	1·198 (3)
C(21)–C(22)	1·380 (3)	C(21′)–C(22′)	1·377 (4)
C(21)–C(26)	1·390 (4)	C(21′)–C(26′)	1·379 (3)
C(22)–C(23)	1·385 (3)	C(22′)–C(23′)	1·381 (3)
C(23)–C(24)	1·366 (4)	C(23′)–C(24′)	1·370 (4)
C(24)–C(25)	1·356 (4)	C(24′)–C(25′)	1·369 (4)
C(25–C(26)	1·377 (3)	C(25′)–C(26′)	1·385 (4)

O(1)–C(1)–C(11)	109·8 (2)	O(1′)–C(1′)–C(11′)	107·2 (2)
C(12)–C(11)–C(1)	119·6 (2)	C(12′)–C(11′)–C(1′)	120·1 (2)
C(16)–C(11)–C(1)	120·4 (2)	C(16′)–C(11′)–C(1′)	119·7 (2)
C(16)–C(11)–C(12)	119·9 (2)	C(16′)–C(11′)–C(12′)	120·2 (2)
C(13)–C(12)–C(11)	118·8 (2)	C(13′)–C(12′)–C(11′)	118·6 (2)
C(17)–C(12)–C(11)	122·2 (2)	C(17′)–C(12′)–C(11′)	122·2 (2)
C(17)–C(12)–C(13)	119·0 (2)	C(17′)–C(12′)–C(13′)	119·2 (2)
C(14)–C(13)–C(12)	121·3 (2)	C(14′)–C(13′)–C(12′)	121·1 (2)
C(15)–C(14)–C(13)	120·0 (3)	C(15′)–C(14′)–C(13′)	120·5 (2)
C(16)–C(15)–C(14)	121·0 (2)	C(16′)–C(15′)–C(14′)	120·5 (2)
C(15)–C(16)–C(11)	119·0 (2)	C(15′)–C(16′)–C(11′)	119·1 (2)
C(18)–C(16)–C(11)	122·2 (3)	C(18′)–C(16′)–C(11′)	122·1 (2)
C(18)–C(16)–C(15)	118·7 (2)	C(18′)–C(16′)–C(15′)	118·8 (2)
O(2)–N(1)–C(24)	117·4 (2)	O(2′)–N(1′)–C(24′)	117·8 (2)
O(3)–N(1)–C(24)	117·6 (2)	O(3′)–N(1′)–C(24′)	117·3 (2)
O(3)–N(1)–O(2)	124·9 (2)	O(3′)–N(1′)–O(2′)	124·8 (2)
C(2)–O(1)–C(1)	114·2 (2)	C(2′)–O(1′)–C(1′)	116·1 (2)
C(21)–C(2)–O(1)	112·9 (2)	C(21′)–C(2′)–O(1′)	112·3 (2)
O(21)–C(2)–O(1)	123·5 (2)	O(21′)–C(2′)–O(1′)	123·8 (2)
O(21)–C(2)–C(21)	123·5 (2)	O(21′)–C(2′)–C(21′)	123·9 (2)
C(22)–C(21)–C(2)	123·2 (2)	C(22′)–C(21′)–C(2′)	122·1 (2)
C(26)–C(21)–C(2)	117·5 (2)	C(26′)–C(21′)–C(2′)	118·1 (2)
C(26)–C(21)–C(22)	119·3 (2)	C(26′)–C(21′)–C(22′)	119·9 (2)
C(23)–C(22)–C(21)	120·2 (2)	C(23′)–C(22′)–C(21′)	120·8 (2)
C(24)–C(23)–C(22)	118·6 (2)	C(24′)–C(23′)–C(22′)	118·2 (3)
C(23)–C(24)–N(1)	119·1 (2)	C(23′)–C(24′)–N(1′)	118·8 (2)
C(25)–C(24)–N(1)	118·3 (2)	C(25′)–C(24′)–N(1′)	118·9 (2)
C(25)–C(24)–C(23)	122·7 (2)	C(25′)–C(24′)–C(23′)	122·3 (2)
C(26)–C(25)–C(24)	118·7 (2)	C(26′)–C(25′)–C(24′)	118·9 (2)
C(25)–C(26)–C(21)	120·5 (2)	C(25′)–C(26′)–C(21′)	119·9 (3)

deviation for a typical structure. Thus the conformational problem has indeed been effectively eliminated by introducing the two *ortho*-methyl groups, and by changing to a primary benzylic centre.

Because of this latter change we cannot compare C—O*X* bond lengths for (3*a*)–(3*c*) directly with those for the corresponding 1-arylethanol derivatives. All three are significantly shorter, as expected for bonds to a primary compared with a secondary centre [and longer than expected for bonds to primary aliphatic centres (Allen & Kirby, 1984)]. If we calculate the C—O*X* bond lengths expected for 1-arylethanol derivatives (2), with the same O*X* leaving groups and dihedral angles *abd′*, we find those for (3*a*) and (3*c*) shorter by 0·016 ± 0·002 Å, but that for (3*b*) shorter by 0·034 Å.

This reflects the unexpected observation that the C—O—aryl bond of (3*b*) is no longer than the C—O—alkyl bond of (3*a*). Though it is tempting to ascribe this to a steric effect arising from the juxtaposition of two classically hindered groups (2,6-dimethylphenyl and triphenylmethyl), lengthening the

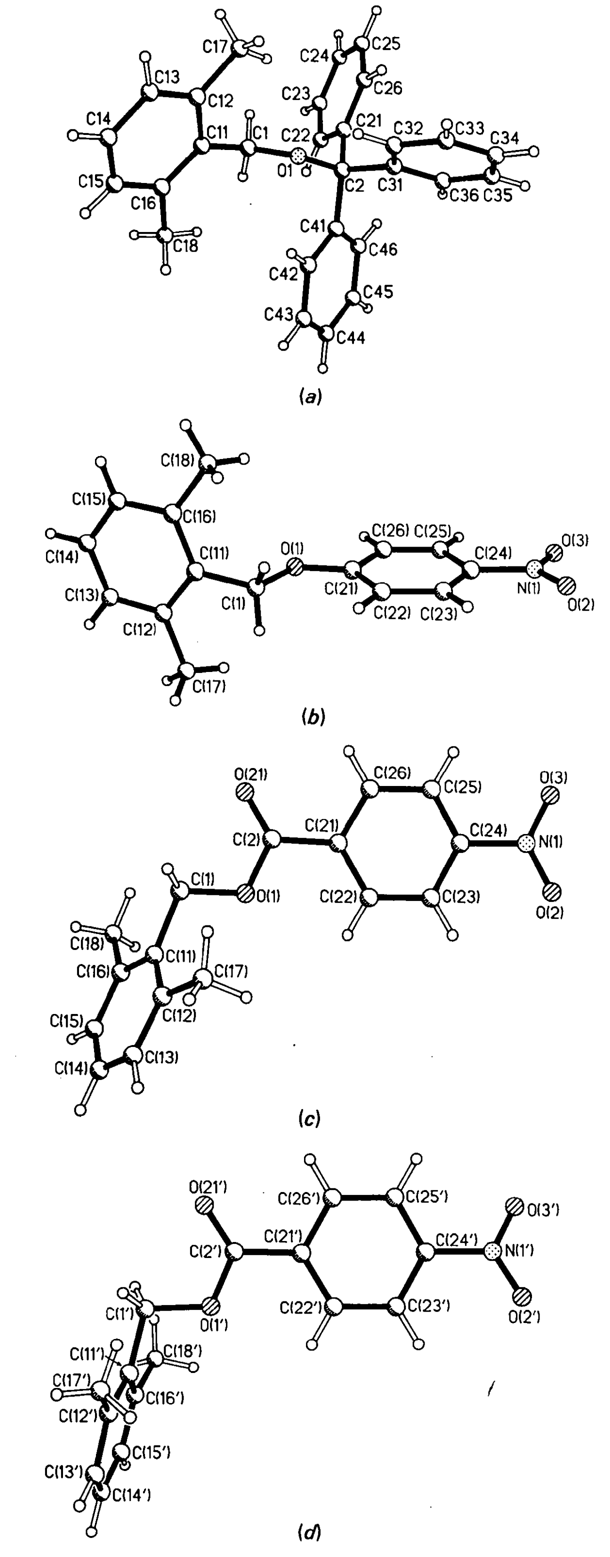

Fig. 1. (*a*) Molecular structure of (3*a*), showing the atom-numbering scheme. (*b*) Molecular structure of (3*b*), showing the atom-numbering scheme. (*c*) Molecular structure of molecule *A* of (3*c*), showing the atom-numbering scheme. (*d*) Molecular structure of molecule *B* of (3*c*), showing the atom-numbering scheme.

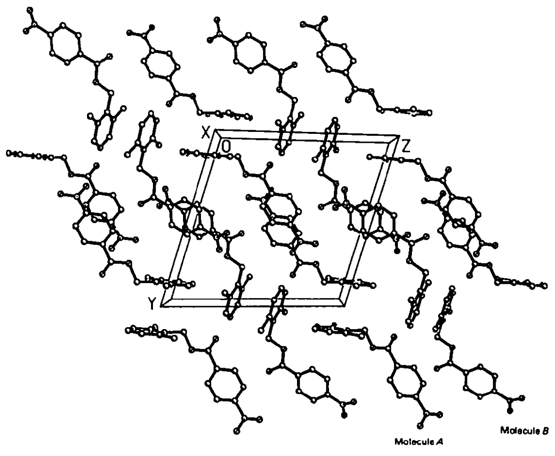

Fig. 2. Packing diagram for (3*c*) (see text).

C—O*R* bond of (3*a*), there are no intramolecular contacts below 4 Å, and the calculation quoted above suggests rather that it is the C—OAr bond of (3*b*) that is unexpectedly short. We have observed this phenomenon previously, for the 4-nitrophenyl ether of 1-phenylethanol [(2), *X* = *p*-nitrophenyl (Jones, Edwards & Kirby, 1986)]. In that case the 4-nitro group was rotated out of plane by 14°, which seems too small to account for a significant shortening of C—OAr. In the case of (3*b*) this is clearly not a factor: the dihedral angle between the ring and NO_2 planes is no more than 2° [torsion angles about C(24)—N(1): −0·7 (4), −1·6 (4), 177·5 (4), 177·3 (4)°].

We conclude that compounds (3) can provide a potentially useful system for examining the effects of ring substitution on C—O*X* bond length in benzylic systems. In the following paper (Jones, Dölle, Kirby & Parker, 1989) we report on our results with a related system.

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

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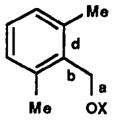
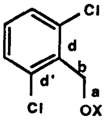
Abstract. 2,6-Dichlorobenzyl triphenylmethyl ether, $C_{26}H_{20}Cl_2O$, (2*a*), $M_r = 418{\cdot}35$, monoclinic, $P2_1$, $a = 9{\cdot}888\,(2)$, $b = 7{\cdot}468\,(2)$, $c = 14{\cdot}298\,(3)$ Å, $\beta = 90{\cdot}04\,(2)°$, $V = 1055{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}32$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ 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 [$= +0{\cdot}84\,(12)$] 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, $\beta = 104{\cdot}49\,(6)°$, $V = 1296{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}52$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ 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, $\beta = 114{\cdot}56\,(2)°$, $V = 1530{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}61$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ 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*α 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, $2\theta_{\max} = 50°$, 4000 reflections including a full set of Friedel opposites, 3697 unique ($R_{\text{int}} = 0{\cdot}086$, 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, $2\theta_{\max} = 55°$, 3061 reflections, 2969 unique ($R_{\text{int}} = 0{\cdot}037$, 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, $2\theta_{\max} = 55°$, 4399 reflections, 3512 unique ($R_{\text{int}} = 0{\cdot}055$, index ranges h −21 to 20, k 0 to 6, l 0 to 24), 1974 observed.

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

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