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Bond Length and Reactivity.* Structure of 1-Indanol 4-Nitrobenzoate Ester

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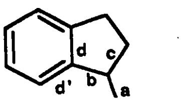
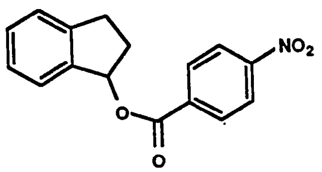
Abstract. 1-Indanol 4-nitrobenzoate, $C_{16}H_{13}NO_4$, $M_r = 283{\cdot}28$, triclinic, $P\bar{1}$, $a = 8{\cdot}116\,(1)$, $b = 12{\cdot}784\,(1)$, $c = 13{\cdot}954\,(2)$ Å, $\alpha = 100{\cdot}15\,(1)$, $\beta = 101{\cdot}03\,(1)$, $\gamma = 91{\cdot}66\,(1)°$, $V = 1395{\cdot}9\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}348$ Mg m^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}77$ mm^{-1}, $\mu R = 0{\cdot}24$, $F(000) = 592$, $T = 290$ K, $R = 0{\cdot}058$ for 3196 observed reflections. The asymmetric unit contains two independent molecules with significant conformational differences, and matching differences in C—O(acyl) bond lengths. These are 1·470 (3) and 1·462 (3) Å for molecules (2*A*) and (2*B*), in which the C—O(acyl) bonds make torsion angles with the aromatic ring of 75·2 (3) and 54·7 (4)°, respectively. The C—O*X* bond lengths in three structures of indanol derivatives are consistently shorter than predicted for the corresponding open-chain (1-phenylethyl) compounds, by 0·009±1 Å.

Introduction. We have reported crystal structures for the triphenylmethyl ethers of 1-indanol (1) and its 5-methoxy derivative (Jones, Schmidt-Bäse, Kirby & Parker, 1989). The object was to find a system of fixed conformation, to allow us to separate the effects on benzylic C—O*X* bond lengths of varying conformation and varying leaving group (Edwards, Jones & Kirby, 1986). This first test was successful, in that the two ethers crystallized in almost identical conformations. For the particular leaving group ($OCPh_3$) this provides a sensitive test of the effect on the C—O*X* bond length of the substituent in the aromatic ring.

We report the structure of the *p*-nitrobenzoate ester (2) of 1-indanol, a compound with a much better leaving group. (Other derivatives were made, but no suitable crystals were obtained.)



(1)



(2)

Experimental. The ester (2) was prepared by acylation of the alcohol in dichloromethane containing triethylamine and a catalytic amount of 4-*N*,*N*-dimethylaminopyridine, using *p*-nitrobenzoyl chloride. Crystals, m.p. 349–350 K, were grown by diffusion of hexane into a solution in dichloromethane. Block-shaped single crystal 0·15 × 0·22 × 0·32 mm, Nicolet *R*3*mμ* diffractometer with graphite monochromator, Cu *K*α radiation; unit-cell parameters refined from diffractometer angles of 25 centred reflections ($40 < 2\theta < 50°$); 4377 reflections with $5 < 2\theta < 120°$ (*hkl* range: *h* −10 to 10, *k* 0 to 15, *l* −16 to 16); no significant variations of three standard reflections; empirical absorption correction based on 375 azimuthal scan data and an ellipsoid model, transmission factors 0·34–0·77, 4022 unique reflections with $F > 3\sigma(F)$. Structure solved by centrosymmetric direct methods (*SHELXTL:SOLV*), blocked-cascade least-squares refinement on *F*, anisotropic thermal parameters for all non-H atoms; H atoms fixed to C with C—H 0·96 Å, and allowed to ride on the relevant C atom; each type of H assigned a common isotropic temperature factor; scattering factors from *International Tables for X-ray Crystallography* (1974); 381 parameters, $R = 0{\cdot}058$, $wR = 0{\cdot}065$, $w = [\sigma^2(F_o) +$

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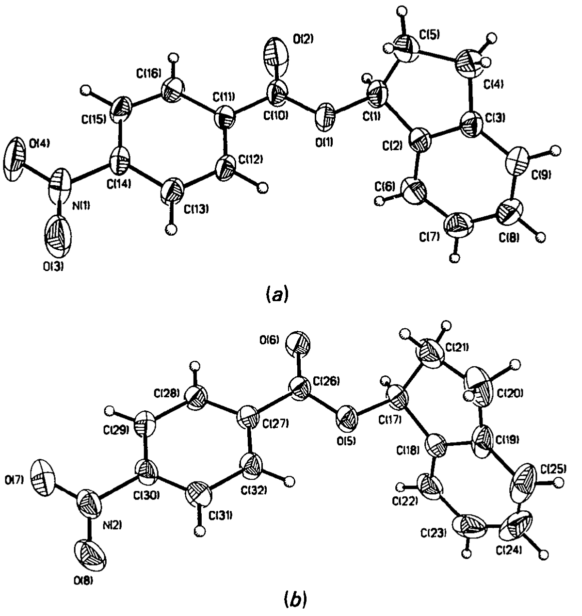
* Previous paper in this series: Jones, Schmidt-Bäse, Kirby & Parker (1989).

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

	x	y	z	U^*
C(1)	9365 (4)	8111 (2)	8260 (2)	76 (1)
C(2)	8208 (3)	8978 (2)	8447 (2)	57 (1)
C(3)	9043 (3)	9962 (2)	8616 (2)	60 (1)
C(4)	10868 (4)	9872 (3)	8560 (3)	82 (1)
C(5)	10997 (4)	8701 (3)	8180 (3)	115 (2)
C(6)	6505 (4)	8884 (3)	8480 (2)	78 (1)
C(7)	5700 (4)	9801 (3)	8702 (3)	85 (2)
C(8)	6539 (4)	10787 (3)	8862 (3)	85 (1)
C(9)	8205 (4)	10868 (2)	8830 (3)	81 (1)
O(1)	8649 (3)	7397 (1)	7324 (1)	70 (1)
C(10)	9024 (4)	6390 (2)	7247 (2)	73 (1)
O(2)	9833 (4)	6037 (2)	7898 (2)	149 (1)
C(11)	8332 (3)	5749 (2)	6243 (2)	55 (1)
C(12)	7228 (3)	6145 (2)	5529 (2)	54 (1)
C(13)	6615 (3)	5516 (2)	4607 (2)	58 (1)
C(14)	7147 (3)	4494 (2)	4419 (2)	55 (1)
C(15)	8257 (3)	4087 (2)	5116 (2)	62 (1)
C(16)	8828 (3)	4709 (2)	6027 (2)	66 (1)
N(1)	6476 (3)	3818 (2)	3445 (2)	76 (1)
O(3)	5461 (4)	4178 (2)	2846 (2)	117 (1)
O(4)	6939 (4)	2921 (2)	3294 (2)	118 (1)
C(17)	2887 (3)	3313 (2)	7822 (2)	63 (1)
C(18)	4464 (4)	3536 (2)	8594 (2)	61 (1)
C(19)	4126 (4)	3402 (2)	9513 (2)	77 (1)
C(20)	2295 (5)	3103 (3)	9415 (3)	98 (2)
C(21)	1495 (4)	3312 (3)	8397 (3)	88 (2)
C(22)	6039 (4)	3821 (3)	8461 (3)	87 (1)
C(23)	7327 (5)	3969 (3)	9293 (4)	125 (2)
C(24)	7005 (7)	3830 (3)	10210 (4)	137 (2)
C(25)	5418 (7)	3560 (3)	10312 (3)	113 (2)
O(5)	2996 (2)	2257 (1)	7225 (1)	63 (1)
C(26)	2019 (3)	2036 (2)	5323 (2)	55 (1)
O(6)	1009 (3)	2612 (2)	5998 (2)	77 (1)
C(27)	2345 (3)	987 (2)	5755 (2)	50 (1)
C(28)	1706 (3)	761 (2)	4738 (2)	61 (1)
C(29)	2006 (3)	−190 (2)	4174 (2)	64 (1)
C(30)	2925 (3)	−905 (2)	4644 (2)	54 (1)
C(31)	3568 (3)	−707 (2)	5642 (2)	61 (1)
C(32)	3282 (3)	253 (2)	6203 (2)	57 (1)
N(2)	3271 (3)	−1913 (2)	4041 (2)	68 (1)
O(7)	2468 (3)	−2158 (2)	3192 (2)	107 (1)
O(8)	4325 (3)	−2453 (2)	4415 (2)	88 (1)

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



(a)

(b)

Fig. 1. Molecular conformations of the two independent molecules of (2): (a) molecule A, (b) molecule B. Thermal motion is represented as 30% probability ellipsoids.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

C(1)–C(2)	1·493 (4)	C(1)–C(5)	1·538 (5)
C(1)–O(1)	1·462 (3)	C(2)–C(3)	1·372 (4)
C(2)–C(6)	1·394 (4)	C(3)–C(4)	1·504 (4)
C(3)–C(9)	1·377 (4)	C(4)–C(5)	1·511 (5)
C(6)–C(7)	1·375 (5)	C(7)–C(8)	1·377 (5)
C(8)–C(9)	1·363 (5)	O(1)–C(10)	1·322 (3)
C(10)–O(2)	1·181 (4)	C(10)–C(11)	1·489 (4)
C(11)–C(12)	1·384 (4)	C(11)–C(16)	1·400 (4)
C(12)–C(13)	1·384 (3)	C(13)–C(14)	1·385 (4)
C(14)–C(15)	1·378 (4)	C(14)–N(1)	1·472 (3)
C(15)–C(16)	1·363 (4)	N(1)–O(3)	1·217 (4)
N(1)–O(4)	1·213 (3)	C(17)–C(18)	1·491 (4)
C(17)–C(21)	1·506 (5)	C(17)–O(5)	1·470 (3)
C(18)–C(19)	1·398 (4)	C(18)–C(22)	1·375 (5)
C(19)–C(20)	1·499 (5)	C(19)–C(25)	1·358 (5)
C(20)–C(21)	1·517 (5)	C(22)–C(23)	1·387 (6)
C(23)–C(24)	1·395 (9)	C(24)–C(25)	1·363 (8)
O(5)–C(26)	1·332 (3)	C(26)–O(6)	1·195 (3)
C(26)–C(27)	1·491 (3)	C(27)–C(28)	1·390 (4)
C(27)–C(32)	1·384 (4)	C(28)–C(29)	1·382 (4)
C(29)–C(30)	1·373 (4)	C(30)–C(31)	1·365 (4)
C(30)–N(2)	1·475 (3)	C(31)–C(32)	1·386 (4)
N(2)–O(7)	1·220 (3)	N(2)–O(8)	1·214 (3)

C(2)–C(1)–C(5)	104·1 (3)	C(2)–C(1)–O(1)	109·3 (2)
C(5)–C(1)–O(1)	110·6 (3)	C(1)–C(2)–C(3)	111·1 (2)
C(1)–C(2)–C(6)	128·4 (3)	C(3)–C(2)–C(6)	120·6 (3)
C(2)–C(3)–C(4)	111·5 (3)	C(2)–C(3)–C(9)	120·1 (3)
C(4)–C(3)–C(9)	128·5 (3)	C(3)–C(4)–C(5)	104·1 (2)
C(1)–C(5)–C(4)	107·5 (3)	C(2)–C(6)–C(7)	118·3 (3)
C(6)–C(7)–C(8)	121·0 (3)	C(7)–C(8)–C(9)	120·2 (3)
C(3)–C(9)–C(8)	119·9 (3)	C(1)–O(1)–C(10)	117·0 (2)
O(1)–C(10)–O(2)	123·8 (3)	O(1)–C(10)–C(11)	112·6 (2)
O(2)–C(10)–C(11)	123·6 (3)	C(10)–C(11)–C(12)	122·5 (2)
C(10)–C(11)–C(16)	117·9 (2)	C(12)–C(11)–C(16)	119·6 (2)
C(11)–C(12)–C(13)	120·2 (2)	C(12)–C(13)–C(14)	118·4 (2)
C(13)–C(14)–C(15)	122·2 (2)	C(13)–C(14)–N(1)	118·5 (2)
C(15)–C(14)–N(1)	119·3 (2)	C(14)–C(15)–C(16)	118·7 (2)
C(11)–C(16)–C(15)	120·8 (3)	C(14)–N(1)–O(3)	118·5 (2)
C(14)–N(1)–O(4)	117·7 (2)	O(3)–N(1)–O(4)	123·7 (2)
C(18)–C(17)–C(21)	104·9 (2)	C(18)–C(17)–O(5)	106·9 (2)
C(21)–C(17)–O(5)	111·5 (2)	C(17)–C(18)–C(19)	109·7 (3)
C(17)–C(18)–C(22)	127·1 (3)	C(19)–C(18)–C(22)	123·2 (3)
C(18)–C(19)–C(20)	110·3 (3)	C(18)–C(19)–C(25)	118·4 (4)
C(20)–C(19)–C(25)	131·3 (4)	C(19)–C(20)–C(21)	104·0 (3)
C(17)–C(21)–C(20)	106·4 (3)	C(18)–C(22)–C(23)	116·7 (4)
C(22)–C(23)–C(24)	120·5 (4)	C(23)–C(24)–C(25)	120·9 (4)
C(19)–C(25)–C(24)	120·3 (4)	C(17)–O(5)–C(26)	116·8 (2)
O(5)–C(26)–O(6)	124·3 (2)	O(5)–C(26)–C(27)	112·0 (2)
O(6)–C(26)–C(27)	123·7 (2)	C(26)–C(27)–C(28)	118·0 (2)
C(26)–C(27)–C(32)	122·3 (2)	C(28)–C(27)–C(32)	119·7 (2)
C(27)–C(28)–C(29)	120·3 (3)	C(28)–C(29)–C(30)	118·5 (2)
C(29)–C(30)–C(31)	122·6 (2)	C(29)–C(30)–N(2)	118·5 (2)
C(31)–C(30)–N(2)	118·8 (2)	C(30)–C(31)–C(32)	118·8 (3)
C(27)–C(32)–C(31)	120·1 (2)	C(30)–N(2)–O(7)	117·8 (2)
C(30)–N(2)–O(8)	118·5 (2)	O(7)–N(2)–O(8)	123·7 (2)

$0{\cdot}00079F_o{}^2]^{-1}$, for all data $R = 0{\cdot}071$, $wR = 0{\cdot}077$, mean $\Delta/\sigma = 0{\cdot}016$, max. 0·080, $\Delta\rho$ variations in final difference map from $+0{\cdot}25$ to $-0{\cdot}22$ e $Å^{-3}$, programs *SHELXTL* package (Sheldrick, 1985).*

Discussion. Final atom coordinates and equivalent isotropic temperature factors are presented in Table 1, and thermal-ellipsoid plots of (2), showing the atom-numbering schemes for the two molecules, appear in Fig. 1(*a,b*). Bond lengths and angles are given in Table 2.

The ester (2) crystallizes with two independent molecules in the asymmetric unit. Their conformations

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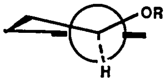
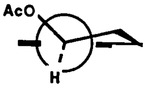
* Lists of H-atom coordinates and $U_{\rm iso}$ values, structure factors and anisotropic thermal parameters and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51327 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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).

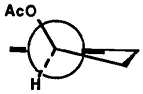
Evidently tying back the benzylic substituent group in a five-membered ring fails to produce the desired effect of fixing the conformation about the ring—C_α bond when different leaving groups are involved. The three structures have torsion angles *abd'* of 75·2 (3), 54·7 (4) (ester) and −36·2 (3)° (ether), 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*), $C_{28}H_{26}O$, $M_r = 378{\cdot}5$, orthorhombic, $Pca2_1$, $a = 28{\cdot}271$ (2), $b = 9{\cdot}981$ (1), $c = 7{\cdot}668$ (1) Å, $V = 2163{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}16$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}46$ mm^{-1}, $F(000) = 808$, $T = 293$ K, $R = 0{\cdot}056$ for 2768 unique observed reflections. 2,6-Dimethylbenzyl 4-nitrophenyl ether (3*b*), $C_{15}H_{15}NO_3$, $M_r = 257{\cdot}3$, monoclinic, $P2_1/c$, $a = 8{\cdot}691$ (1), $b = 11{\cdot}506$ (1), $c = 13{\cdot}700$ (2) Å, $\beta = 94{\cdot}90$ (1)°, V

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

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