a preference for a small torsion angle *abd*. The two *meta*-CF_3 groups ($\sigma_m = 0{\cdot}415$, 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)° and 1·443 (3) Å, respectively] are expected.

We have thus defined conditions for controlling the conformation of the C—O*X* 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—O*X* bond can be directed into a near-perpendicular conformation by introducing two *ortho*-methyl groups (Jones, Dölle, Kirby & Parker, 1989*a*). 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) Å and 5·4 (4)° for (2) compare with values of 1·467 (2) Å and 86·3 (2)° for molecule *B* of the *p*-nitrobenzoate of 2,6-dimethylbenzyl alcohol (Jones *et al.*, 1989*a*).

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

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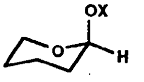
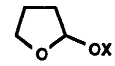
Abstract. $C_{10}H_{11}NO_4$, $M_r = 209{\cdot}20$, monoclinic, $P2_1/c$, $a = 9{\cdot}767\,(2)$, $b = 11{\cdot}942\,(2)$, $c = 8{\cdot}522\,(2)$ Å, $\beta = 92{\cdot}06\,(2)°$, $V = 993{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}40$ Mg m^{-3}, $F(000) = 440$, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}1$ mm^{-1}, $T = 293$ K. The structure was refined to $R = 0{\cdot}052$ 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) Å longer than the endocyclic C(2)—O(1) = 1·392 (3) Å. Both are closely similar to those observed for a comparable tetrahydropyranyl acetal.

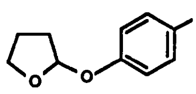
Introduction. We have demonstrated linear relationships between bond length and reactivity in several series of acetals (Jones & Kirby, 1979, 1984, 1986; Briggs, Glenn, Jones, Kirby & Ramaswamy, 1984). As a general rule, the longer the C—O bond in a given series, the faster it breaks: furthermore, the more reactive the system, the more sensitive is the length of the bond that breaks to the leaving group capability of the group O*X* (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).



(1)



(2)



(3)

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

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Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

	x	y	z	U_{eq}*
O(1)	6472 (1)	7257 (1)	4961 (2)	53 (1)
C(2)	5526 (2)	7934 (2)	4148 (2)	45 (1)
C(3)	6242 (2)	9013 (2)	3796 (2)	50 (1)
C(4)	7219 (2)	9134 (2)	5208 (3)	55 (1)
C(5)	7600 (2)	7940 (2)	5571 (3)	61 (1)
O(2)	4404 (1)	8213 (1)	5123 (2)	51 (1)
C(11)	3494 (2)	7408 (2)	5510 (2)	42 (1)
C(12)	2378 (2)	7777 (2)	6332 (2)	49 (1)
C(13)	1403 (2)	7039 (2)	6797 (2)	50 (1)
C(14)	1532 (2)	5919 (2)	6420 (2)	45 (1)
C(15)	2633 (2)	5529 (2)	5613 (2)	48 (1)
C(16)	3626 (2)	6273 (2)	5159 (2)	46 (1)
N	485 (2)	5131 (2)	6896 (2)	60 (1)
O(41)	593 (2)	4148 (1)	6519 (2)	72 (1)
O(42)	−471 (2)	5483 (2)	7629 (3)	100 (1)

* Equivalent isotropic U calculated from anisotropic U as $\frac{1}{3}$ of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Molecular geometry for* (3) *with e.s.d.'s in parentheses*

(*a*) Bond lengths (Å)

C(2)—O(1)	1·392 (3)	C(2)—C(3)	1·501 (4)
C(2)—O(2)	1·439 (3)	C(3)—C(4)	1·515 (4)
C(4)—C(5)	1·503 (4)	C(5)—O(1)	1·452 (4)
C(11)—O(2)	1·358 (3)	C(11)—C(12)	1·388 (4)
C(11)—C(16)	1·395 (4)	C(12)—C(13)	1·367 (4)
C(13)—C(14)	1·382 (4)	C(14)—C(15)	1·378 (4)
C(14)—N	1·459 (4)	C(15)—C(16)	1·380 (4)
N—O(41)	1·222 (4)	N—O(42)	1·217 (4)

(*b*) Bond angles (°)

C(2)—O(1)—C(5)	109·5 (2)	O(1)—C(2)—C(3)	107·0 (3)
O(1)—C(2)—O(2)	110·6 (3)	C(3)—C(2)—O(2)	106·7 (3)
C(2)—C(3)—C(4)	102·0 (3)	C(3)—C(4)—C(5)	102·5 (3)
O(1)—C(5)—C(4)	106·2 (3)	C(2)—O(2)—C(11)	119·7 (2)
O(2)—C(11)—C(12)	115·5 (3)	O(2)—C(11)—C(16)	124·7 (3)
C(12)—C(11)—C(16)	119·8 (3)	C(11)—C(12)—C(13)	120·6 (3)
C(12)—C(13)—C(14)	119·1 (3)	C(13)—C(14)—C(15)	121·5 (3)
C(13)—C(14)—N	119·3 (3)	C(15)—C(14)—N	119·2 (3)
C(14)—C(15)—C(16)	119·4 (3)	C(11)—C(16)—C(15)	119·6 (3)
C(14)—N—O(41)	118·6 (3)	C(14)—N—O(42)	118·5 (3)
O(41)—N—O(42)	122·9 (3)		

(*c*) Selected torsion angles (°)

C(5)—O(1)—C(2)—C(3)	17·4 (3)	C(5)—O(1)—C(2)—O(2)	−98·4 (3)
C(2)—O(1)—C(5)—C(4)	5·5 (3)	O(1)—C(2)—C(3)—C(4)	−32·7 (3)
O(2)—C(2)—C(3)—C(4)	85·7 (3)	O(1)—C(2)—O(2)—C(11)	−70·0 (3)
C(3)—C(2)—O(2)—C(11)	174·0 (3)	C(2)—C(3)—C(4)—C(5)	34·5 (3)
C(3)—C(4)—C(5)—O(1)	−25·4 (3)	C(2)—O(2)—C(11)—C(12)	−174·3 (3)
C(2)—O(2)—C(11)—C(16)	6·6 (4)	C(13)—C(14)—N—O(42)	−·6 (4)
C(13)—C(14)—N—O(41)	178·1 (3)	C(15)—C(14)—N—O(42)	178·9 (3)
C(15)—C(14)—N—O(41)	−2·4 (4)		

It was of interest to compare the tetrahydropyranyl acetals (1) with the corresponding tetrahydrofuranyl acetals, (2), which might be expected to show subtle differences in behaviour. In the event several simple tetrahydrofuranyl acetals (2) – unlike the large number of furanose sugars in the crystallographic literature – gave crystals unsuitable for structure analysis. This may be a consequence of the conformational flexibility of the unsubstituted five-membered ring. We report the structure of one simple tetrahydropyranyl acetal, the *p*-nitrophenyl derivative (3).

Experimental. The acetal (3) was prepared from 2-chlorotetrahydrofuran by the method of Cruse, Jonkers, Dert & van der Gen (1979). Liquid diffusion of pentane into a solution of (3) in diethyl ether gave pale yellow prisms, m.p. 351–352 K.

A crystal *ca* 0·6 × 0·45 × 0·45 mm was mounted in a glass capillary. 2397 profile-fitted intensities (Clegg, 1981) were recorded on a Stoe–Siemens four-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{max}$ 55°). Three check reflections showed no significant intensity change. Merging equivalents gave 2269 unique reflections (R_{int} 0·021, index ranges after merging h −12 to 12, k 0 to 15, l 0 to 11), of which 1531 with $F > 4\sigma(F)$ were used for all calculations *via* program system *SHELXTL* (Sheldrick, 1986). Cell constants were refined from 2θ values of 67 reflections in the range 20–23°.

The structure was solved by routine direct methods and subjected to cascade least-squares refinement on F. The final R value was 0·052, with wR 0·054, for 136 parameters (all non-H atoms anisotropic, H atoms included using a riding model). The weighting scheme was $w^{-1} = \sigma^2(F) + 0{\cdot}0003F^2$. $S = 1{\cdot}7$, max. Δ/σ 0·03, max. $\Delta\rho$ within $\pm 0{\cdot}18$ e Å^{-3}. Scattering factors were those stored in the *SHELXTL* program.

Discussion. Final atom coordinates are given in Table 1, and derived parameters in Table 2.* A thermal-

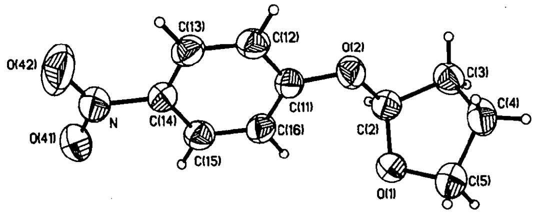

Fig. 1. Molecular structure of (3), showing the atom-numbering scheme.

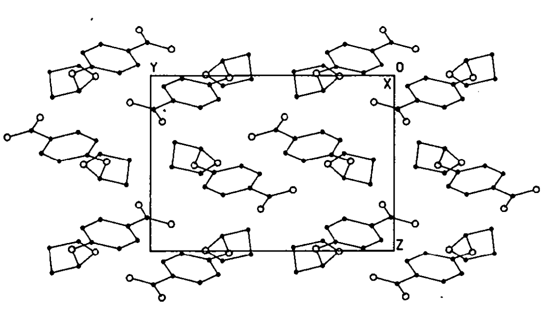

Fig. 2. Packing diagram for (3). The shortest intermolecular contact not involving H atoms is O(41)—N, 3·18 Å (N at −x, 1−y, 1−z).

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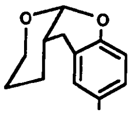
* Lists of H-atom coordinates and U_{iso} values, structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51407 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

ellipsoid plot of (3) is shown as Fig. 1. The packing diagram (Fig. 2) shows no unusual features. (3) crystallizes with the tetrahydrofuran ring in a distorted envelope conformation, with intra-annular torsion angles C(3)—C(4), C(4)—C(5) *etc.* of 34·5 (3), −25·4 (3), 5·5 (3), 17·4 (3) and −32·7 (3)°. In terms of the parameters defined for five-membered rings by Altona & Sundaralingam (1972), the amplitude τ_m and phase angle (P) of pseudorotation are −35·3 and 169·7°, respectively; these values fall in the middle of a range commonly observed for the ribose rings of nucleosides and nucleotides. The *O*-aryl substituent is pseudo-axial, as expected, with torsion angles about the central C—O bonds of the C—O—C—OAr unit of −98·4 (3) and −70·0 (3)°, close to optimal for the n–$\sigma^*_{\text{C—OAr}}$ orbital overlap which is the basis for the anomeric effect (Kirby, 1983).

The lengths of these two C—O bonds [n = 1·392 (3), x = 1·439 (3) Å] are very different, reflecting the unsymmetrical structure of this alkyl aryl acetal. The absolute magnitudes are closely similar to those [1·385 (4), 1·448 (4) Å] measured for the *p*-nitrophenyl tetrahydropyranyl acetal (4) (Jones, Kennard, Kirby & Martin, 1979).



(4)

A simple comparison of this sort can tell us little about bond length and reactivity, and it is the sensitivity of the C—OX bond length to structural change which is the more widely applicable parameter (Jones & Kirby, 1986). But the similar C—OAr bond lengths in (3) and (4) are reflected in similar reactivities. Data are available for the spontaneous hydrolysis of 2-(4-nitrophenoxy)tetrahydropyran as a function of temperature (Fife & Brod, 1970), and for the same reaction of a series of 2-aryloxytetrahydrofurans (2) at 358·15 K (Lönnberg & Pohjola, 1976). Extrapolated rates for the two *p*-nitrophenyl acetals at 358·15 K are almost identical.

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(2*SR*,6*RS*)-6-Phenyl-2-phenylmethoxy-6-trifluoromethyltetrahydropyran-4-one*

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(*Received* 18 *July* 1988; *accepted* 21 *September* 1988)

Abstract. $C_{19}H_{17}F_3O_3$, M_r = 350·34, triclinic, $P\bar{1}$, a = 9·293 (2), b = 10·392 (3), c = 10·605 (3) Å, α = 66·60 (2), β = 70·88 (2), γ = 66·51 (2)°, V = 844·4 Å^3, Z = 2, D_x = 1·38 Mg m^{-3}, $F(000)$ = 364, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·11 mm^{-1}, T = 293 K. The structure was refined to R = 0·045 for 2417 unique observed reflections. The tetrahydropyran ring adopts a conformation close to a classical boat, as a result of conflicting steric and stereoelectronic effects. The C—O

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* Crystal Structures of Acetals. 27. Part 26: Jones, Kirby & Ryder (1989).

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