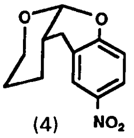
ellipsoid plot of (3) is shown as Fig. 1. The packing diagram (Fig. 2) shows no unusual features. (3) crystallizes with the tetrahydrofuran ring in a distorted envelope conformation, with intra-annular torsion angles C(3)—C(4), C(4)—C(5) *etc.* of 34·5 (3), −25·4 (3), 5·5 (3), 17·4 (3) and −32·7 (3)°. 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—O*X* 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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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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Table 1. *Atom coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

	x	y	z	U_{eq}*
O(1)	1611 (1)	5617 (1)	8406 (1)	46 (1)
C(2)	3291 (2)	4844 (2)	8115 (2)	38 (1)
C(3)	3693 (2)	3796 (2)	7272 (2)	43 (1)
C(4)	2470 (2)	3036 (2)	7639 (2)	47 (1)
O(4)	2831 (2)	1778 (1)	7659 (2)	70 (1)
C(5)	760 (3)	3959 (2)	7946 (2)	55 (1)
C(6)	610 (2)	5540 (2)	7681 (2)	48 (1)
O(6)	998 (2)	6208 (1)	6224 (1)	48 (1)
C(10)	512 (3)	7788 (2)	5853 (2)	57 (1)
C(11)	1030 (2)	8430 (2)	4305 (2)	48 (1)
C(12)	112 (3)	8647 (2)	3395 (2)	61 (1)
C(13)	546 (3)	9276 (3)	1981 (3)	78 (1)
C(14)	1906 (4)	9712 (2)	1448 (3)	77 (1)
C(15)	2825 (3)	9508 (2)	2338 (3)	71 (1)
C(16)	2388 (3)	8864 (2)	3755 (3)	60 (1)
C(21)	4240 (2)	5947 (2)	7427 (2)	40 (1)
C(22)	3569 (3)	7334 (2)	7610 (2)	51 (1)
C(23)	4422 (3)	8337 (2)	7002 (2)	64 (1)
C(24)	5944 (3)	7960 (3)	6222 (2)	69 (1)
C(25)	6632 (3)	6583 (3)	6059 (2)	64 (1)
C(26)	5789 (2)	5575 (2)	6660 (2)	51 (1)
C(27)	3668 (3)	3920 (2)	9572 (2)	48 (1)
F(1)	2915 (2)	2888 (1)	10211 (1)	67 (1)
F(2)	3215 (2)	4725 (1)	10425 (1)	64 (1)
F(3)	5230 (2)	3207 (1)	9510 (1)	67 (1)

* Equivalent isotropic $U_{eq} = \frac{1}{3}$ of the trace of the orthogonalized U_{ij} tensor.

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

(*a*) Bond lengths (Å)

C(2)—O(1)	1·435 (2)	C(2)—C(3)	1·428 (3)
C(2)—C(21)	1·534 (3)	C(2)—C(27)	1·531 (3)
C(3)—C(4)	1·530 (2)	C(4)—O(4)	1·500 (3)
C(4)—C(5)	1·206 (3)	C(5)—C(6)	1·498 (3)
C(6)—O(1)	1·509 (3)	C(6)—O(6)	1·408 (2)
C(10)—O(6)	1·438 (2)	C(10)—C(11)	1·497 (3)
C(11)—C(12)	1·387 (4)	C(11)—C(16)	1·377 (3)
C(12)—C(13)	1·369 (3)	C(13)—C(14)	1·381 (5)
C(14)—C(15)	1·374 (5)	C(15)—C(16)	1·374 (3)
C(21)—C(22)	1·390 (3)	C(21)—C(26)	1·386 (2)
C(22)—C(23)	1·385 (4)	C(23)—C(24)	1·374 (3)
C(24)—C(25)	1·371 (4)	C(25)—C(26)	1·384 (4)
C(27)—F(1)	1·346 (3)	C(27)—F(2)	1·328 (3)
C(27)—F(3)	1·334 (2)		

(*b*) Bond angles (°)

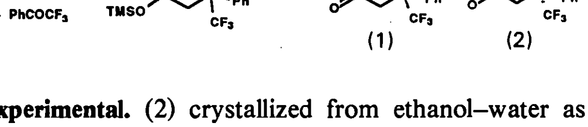
C(2)—O(1)—C(6)	117·5 (2)	O(1)—C(2)—C(3)	113·0 (2)
O(1)—C(2)—C(21)	109·7 (1)	C(3)—C(2)—C(21)	113·0 (1)
O(1)—C(2)—C(27)	103·5 (1)	C(3)—C(2)—C(27)	108·4 (1)
C(21)—C(2)—C(27)	108·7 (2)	C(2)—C(3)—C(4)	114·5 (1)
C(3)—C(4)—O(4)	122·5 (2)	C(3)—C(4)—C(5)	115·4 (2)
O(4)—C(4)—C(5)	122·1 (2)	C(4)—C(5)—C(6)	112·0 (2)
O(1)—C(6)—C(5)	110·7 (2)	O(1)—C(6)—O(6)	111·8 (2)
C(5)—C(6)—O(6)	108·5 (2)	C(6)—O(6)—C(10)	112·1 (1)
O(6)—C(10)—C(11)	109·7 (2)	C(10)—C(11)—C(12)	120·2 (2)
C(10)—C(11)—C(16)	121·2 (2)	C(12)—C(11)—C(16)	118·5 (2)
C(11)—C(12)—C(13)	120·8 (3)	C(12)—C(13)—C(14)	119·9 (3)
C(13)—C(14)—C(15)	119·9 (2)	C(14)—C(15)—C(16)	119·7 (3)
C(11)—C(16)—C(15)	121·1 (3)	C(2)—C(21)—C(22)	119·9 (2)
C(2)—C(21)—C(26)	121·4 (2)	C(22)—C(21)—C(26)	118·7 (2)
C(21)—C(22)—C(23)	120·4 (2)	C(22)—C(23)—C(24)	120·1 (2)
C(23)—C(24)—C(25)	120·1 (3)	C(24)—C(25)—C(26)	120·2 (2)
C(21)—C(26)—C(25)	120·5 (2)	C(2)—C(27)—F(1)	111·5 (2)
C(2)—C(27)—F(2)	112·7 (1)	F(1)—C(27)—F(2)	106·4 (1)
C(2)—C(27)—F(3)	111·8 (1)	F(1)—C(27)—F(3)	106·6 (1)
F(2)—C(27)—F(3)	107·4 (2)		

(*c*) Selected torsion angles (°)

C(6)—O(1)—C(2)—C(3)	−11·4 (3)	C(6)—O(1)—C(2)—C(21)	115·6 (3)
C(6)—O(1)—C(2)—C(27)	−128·5 (3)	C(2)—O(1)—C(6)—C(5)	56·9 (3)
C(2)—O(1)—C(6)—O(6)	−64·1 (3)	O(1)—C(2)—C(3)—C(4)	−36·4 (3)
C(21)—C(2)—C(3)—C(4)	−161·7 (2)	C(27)—C(2)—C(3)—C(4)	77·7 (3)
O(1)—C(2)—C(21)—C(22)	22·3 (3)	O(1)—C(2)—C(21)—C(26)	−160·0 (3)
C(3)—C(2)—C(21)—C(22)	149·4 (3)	C(3)—C(2)—C(21)—C(26)	−33·0 (3)
C(27)—C(2)—C(21)—C(22)	−90·2 (3)	C(27)—C(2)—C(21)—C(26)	87·4 (3)
O(1)—C(2)—C(27)—F(1)	65·8 (3)	O(1)—C(2)—C(27)—F(2)	−53·8 (3)
O(1)—C(2)—C(27)—F(3)	−174·9 (3)	C(3)—C(2)—C(27)—F(1)	−54·4 (3)
C(3)—C(2)—C(27)—F(2)	−174·0 (3)	C(3)—C(2)—C(27)—F(3)	64·8 (3)
C(21)—C(2)—C(27)—F(1)	−177·6 (2)	C(21)—C(2)—C(27)—F(2)	62·8 (3)
C(21)—C(2)—C(27)—F(3)	−58·3 (3)	C(2)—C(3)—C(4)—O(4)	−143·1 (3)
C(2)—C(3)—C(4)—C(5)	38·3 (3)	C(3)—C(4)—C(5)—C(6)	5·6 (3)
O(4)—C(4)—C(5)—C(6)	−172·9 (3)	C(4)—C(5)—C(6)—O(1)	−52·5 (3)
C(4)—C(5)—C(6)—O(6)	70·5 (3)	O(1)—C(6)—O(6)—C(10)	−72·0 (3)
C(5)—C(6)—O(6)—C(10)	165·6 (3)	C(6)—O(6)—C(10)—C(11)	177·1 (3)
O(6)—C(10)—C(11)—C(12)	82·4 (3)	O(6)—C(10)—C(11)—C(16)	−99·8 (3)

bond lengths at the acetal centre differ, with the endocyclic bond C(6)—O(1) = 1·428 (3) Å significantly longer than the exocyclic C(6)—O(6) = 1·408 (2) Å.

Introduction. As part of a synthesis of acetals of biological interest we carried out the hetero Diels–Alder reaction of phenyl trifluoromethyl ketone with 1-benzyloxy-3-trimethylsilyloxybutadiene (Ryder, 1986). Fluoride work-up followed by flash column chromatography on silica gel gave a 61% yield of a 5:1 mixture of diastereoisomers (1). Fractional crystallization from hexane separated the diastereoisomers, but the assignment of their stereochemistry was less unambiguous than normal for tetrahydropyranyl acetals because neither showed an axial proton signal in the ^{1}H NMR. In view of our continuing interest in acetal structure (Briggs, Glenn, Jones, Kirby & Ramaswamy, 1984) we have determined the crystal structure of the major isomer (2). Its unusual conformation explains the spectroscopic observations.



(1) (2)

Experimental. (2) crystallized from ethanol–water as colourless tablets, m.p. 357·5–358·5 K. A crystal *ca* 0·7 × 0·55 × 0·4 mm was mounted in a glass capillary. 3753 profile-fitted intensities (Clegg, 1981) were recorded on a Stoe–Siemens four-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{max}$ 50°). Three check reflections showed no significant intensity change. Merging equivalents gave 2966 unique reflections (R_{int} 0·018, index ranges after merging h −11 to 11, k −12 to 12, l 0 to 12), of which 2417 with $F > 4\sigma(F)$ were used for all calculations *via* program system *SHELX* (Sheldrick, 1976). Cell constants were refined from 2θ values of 51 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 0·045, with $wR = 0{\cdot}053$; all non-H atoms were anisotropic, and H atoms were included using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F) + 0{\cdot}0003F^2$. 226 parameters; $S = 1{\cdot}9$, max. Δ/σ 0·002, max. $\Delta\rho$ within $\pm 0{\cdot}18$ e Å^{-3}. Scattering factors were those stored in the *SHELX* program.

Discussion. Final atom coordinates and molecular geometry are given in Tables 1 and 2,* and a thermal-ellipsoid plot of (2) appears as Fig. 1. The molecular packing is shown in Fig. 2. The tetrahydropyran ring adopts a conformation close to a classical boat, with C(6) as the prow and C(3) at the stern. The geometry is that of a regular boat around C(6), with only a slight twist in the middle, and some flattening at C(3). Ring torsion angles are compared with those for a symmetrical boat in Fig. 3.

A non-chair conformation is not unexpected, since two of the ring substituents have conflicting steric and stereoelectronic requirements. C_6H_5 has a slightly stronger equatorial preference than CF_3 in cyclohexane [almost 12·5 kJ mol^{-1}, compared with 10·0–10·5 kJ mol^{-1} for CF_3 (Della, 1967)], but in a chair conformation 1,3-*cis*-substituents must both be either axial or equatorial. However, a 2-alkoxy substituent on a tetrahydropyran has a moderately strong axial preference, this being the classical manifestation of the anomeric effect (Kirby, 1983). The result is a compromise (Fig. 1), which allows the *O*-benzyl group to adopt its preferred axial conformation and the phenyl group at C(2) to be (pseudo)equatorial. This sort of compromise usually results in twist-boat conformations [for examples see Kirby (1983) and Petit, Van Nuffel, Van Alsenoy, Lenstra & Giese (1984)]. In the case of (2) the extra structural element appears to be the carbonyl group at C(4), which is staggered with respect to the two protons on C(5), rather than eclipsing one of them as it would do in a twist-boat.

The C—O bond lengths at the acetal centre are those expected for an axial tetrahydropyranyl acetal, with the exocyclic bond the shorter [$x = 1{\cdot}408$ (2), $n = 1{\cdot}428$ (3) Å]. {We recently reported similar bond lengths [$x = 1{\cdot}411$ (6) and 1·406 (6) Å, $n = 1{\cdot}428$ (6) and 1·416 (6) Å] for two model alkyl tetrahydropyranyl acetals (Jones, Sheldrick, Kirby & Briggs, 1985).} This is to be expected since the dihedral angles about the two central acetal C—O bonds [−64·1 (3), −72·0 (3)°] are typical for acetals with conformations determined by the anomeric and *exo*-anomeric effects.

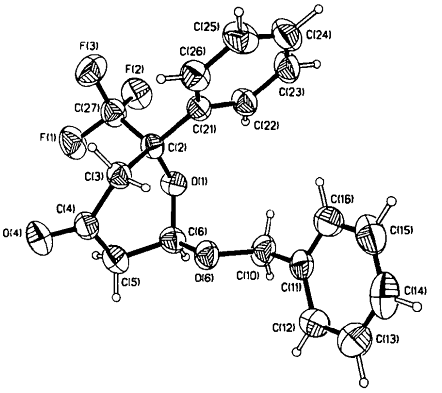


Fig. 1. Molecular structure of (2), showing the atom-numbering scheme.

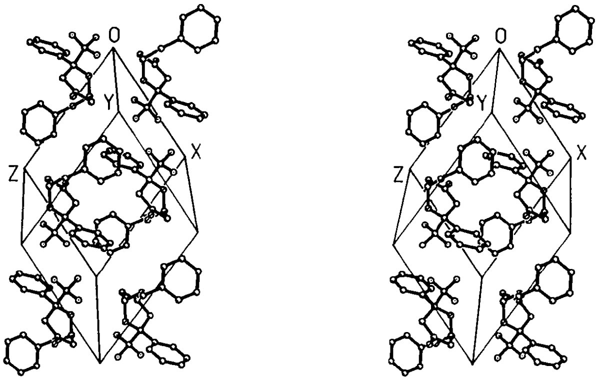


Fig. 2. Packing diagram for (2). The shortest intermolecular contact not involving H is F(3)—F(2) 3·06 Å [F(2) at $1-x$, $1-y$, $2-z$].

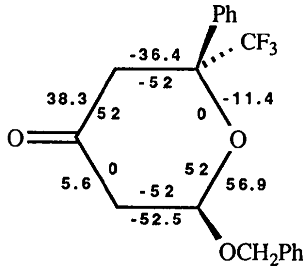


Fig. 3. Torsion angles (e.s.d.'s = 0·3°) for the tetrahydropyran ring of (2) compared with (inside) angles for a symmetrical boat conformation (Dale, 1978).

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* Lists of H-atom coordinates and $U_{\rm iso}$ values, structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51408 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bond Length and Reactivity.* The Pinacol Rearrangement. 1. Redetermination of the Structure of *trans*-Cyclohexane-1,2-diol

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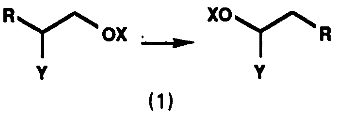
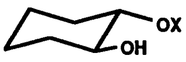
Abstract. $C_6H_{12}O_2$, $M_r = 116·16$, orthorhombic, *Pbca*, $a = 7·8884$ (6), $b = 19·332$ (2), $c = 8·5009$ (8) Å, $V = 1296·4$ Å^3, $Z = 8$, $D_x = 1·19$ Mg m^{-3}, $F(000) = 512$, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 0·08$ mm^{-1}, $T = 293$ K. The structure was refined to $R = 0·042$ for 1288 unique observed reflections. The molecules form hydrogen-bonded layers parallel to the *ac* plane and the two C—O bond lengths are equal at 1·429 (2) Å. The redetermination of the structure originally studied by Sillanpää, Leskelä & Hiltunen [*Acta Chem. Scand. Ser. B* (1984), **38**, 249–254] was undertaken because of our need for precise values of bond lengths, as a basis for detailed structural comparisons.

Introduction. We have found that in suitable systems there is a correlation between the length of a bond and the rate at which it is broken in solution (Jones & Kirby, 1979, 1984). A simple rationalization is that there is a contribution to the ground-state structure of a system R—X from the valence tautomer R^+ X^-, which is apparent as a lengthening of the R—X bond, and is more important the more stable is the 'leaving group' XO$^-$. We use oxygen-based leaving groups XO$^-$, which allow fine-tuning of the leaving group capability, or apparent electronegativity, of the leaving-group oxygen. A convenient measure of this property is the pK_a of its conjugate acid HOX (Kirby, 1987). If this is a valid description of the behaviour of systems R—OX then the bond length and strength must depend equally on the stability of the cation R^+, and we have presented evidence that this is also true (Jones & Kirby, 1986; Edwards, Jones & Kirby, 1986). This raises the intriguing possibility that as we increase the contribution towards the ground-state structure of the R^+ form we may be able to 'see' the structure changing to accommodate the developing positive charge. In principle, therefore, we might expect to see the changes in geometry characteristic of the early stages of familiar heterolytic reactions, and we have reported results of this sort for the S_N1 reaction of a benzylic system (Edwards, Jones & Kirby, 1986).

We are now attempting to apply this principle to simple rearrangement reactions. We have already observed small changes in geometry in the expected direction for oxime derivatives capable of undergoing the Beckmann rearrangement (Edwards, Kirby, Raithby & Jones, 1987). We turn now to the more complicated Wagner–Meerwein rearrangement (1), specifically the familiar pinacol rearrangement [(1), Y = OH].



(1)



(2)

We know it is important that the conformation should remain constant if we are to observe useful correlations for a series of compounds R—OX, so we have prepared a series of derivatives (2) of *trans*-cyclohexane-1,2-diol. We report first the structure of

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