

**Bond Length and Reactivity. Structure of Two Alkyl Oxadecalin Acetals:
2 α -[2-(4-Carboxyphenyl)ethoxy]-*trans*-1-oxadecalin, C₁₈H₂₄O₄ (3), and
2 α -[2,2-Bis(4-chlorophenyl)ethoxy]-*trans*-1-oxadecalin, C₂₃H₂₆Cl₂O₂ (4)*†**

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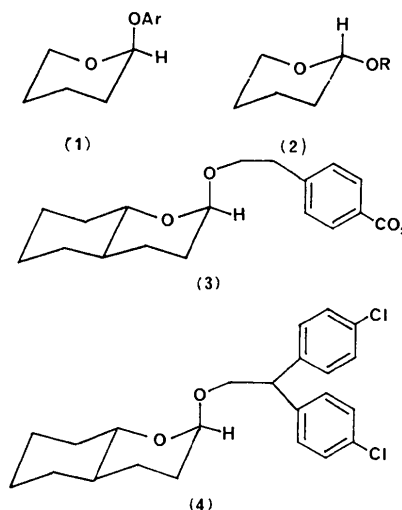
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Abstract. (3): $M_r = 304.39$, monoclinic, $P2_1/n$, $a = 7.558$ (2), $b = 8.894$ (3), $c = 25.256$ (10) Å, $\beta = 93.86$ (4)°, $V = 1694$ (1) Å³, $Z = 4$, $D_x = 1.194$ (2) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.8$ cm⁻¹, $F(000) = 656$, $T = 293$ K, $R = 0.066$ for 1518 observed reflections. (4): $M_r = 405.37$, monoclinic, $P2_1/c$, $a = 19.269$ (4), $b = 8.995$ (2), $c = 13.170$ (3) Å, $\beta = 108.42$ (2)°, $V = 2166$ (1) Å³, $Z = 4$, $D_x = 1.243$ (2) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.0$ cm⁻¹, $F(000) = 856$, $T = 293$ K, $R = 0.064$ for 2237 observed reflections. Both compounds are axial 2-alkoxy-*trans*-1-oxadecalins with approximate (+*sc*, +*sc*) conformations at the acetal centre. The exocyclic C—OR bond lengths are equal within 1 σ : 1.411 (6) for (3), 1.406 (6) Å for (4). These values would not be predicted by extrapolation of our previous linear correlation between bond length and reactivity in axial tetrahydropyranyl acetals [Jones & Kirby (1979). *J. Chem. Soc. Chem. Commun.* pp. 288–289] but are consistent with a Morse function with a substantial linear region.

compounds (1) (Jones & Kirby, 1984). We wished to extend this approach to a 'parent' alkyl tetrahydropyranyl acetal, but alkyl derivatives (1, Ar = alkyl) are almost invariably liquids at ambient temperatures; after many attempts we prepared one such acetal (1, Ar = *N*-phthalimidomethyl), only to find that – the anomeric effect notwithstanding – it had crystallized in the equatorial conformation (2) (Jones, Sheldrick, Briggs & Kirby, 1983). We therefore turned to derivatives of *trans*-1-oxadecalin and bulky alcohols, where the conformations of the axial and equatorial isomers should be fixed by the *trans* ring junction (Chandrasekhar & Kirby, 1983). Eventually we obtained suitable crystals of the 4-carboxyphenylethoxy acetal (3). Shortly afterwards the bis(4-chlorophenyl)ethoxy compound (4), initially an oil, crystallized after standing in the refrigerator for many weeks. Since the C—OR bond length in the 2-alkoxytetrahydropyran system is a key figure for fitting our data to standard expressions like the Morse function (Jones & Kirby, 1984), we have determined crystal structures for both compounds.

Introduction. The linear relationship we observed between the length of the C—OAr bond in a series of aryl tetrahydropyranyl acetals (1) and the free energy of activation for its hydrolytic cleavage (Jones & Kirby, 1979) suggests a possible experimental approach to exploring the reaction coordinate involved (Jones & Kirby, 1984). We regard the lengthening of the acetal C—OAr bond, as ArO⁻ becomes a progressively better leaving group, as marking progress along this reaction coordinate. By making simple assumptions about the transition-state energy for C—OAr cleavage we can relate ground-state energies for the series of



* Crystal Structures of Acetals. 25. Part 24: Jones, Sheldrick, Kirby & Briggs (1985).

† IUPAC names: 4-[2-(3,4,4a,5,6,7,8,8a-octahydro-2H-chromen-2-yloxy)ethyl]benzoic acid and 2-[2,2-bis(4-chlorophenyl)ethoxy]-3,4,4a,5,6,7,8,8a-octahydro-2H-chromene respectively.

Experimental. *Preparation of 2 α -[2-(4-carboxyphenyl)ethoxy]-trans-1-oxadecalin (3).* (3) was obtained by metallation and carboxylation of the corresponding 4-bromophenyl compound [Briggs, 1984: prepared as described below for (4) and purified by preparative thin-layer chromatography]. *n*-Butyllithium (0.26 ml of a 1.5 M solution in hexane, 0.39 mmol) was added over 2 min to a stirred solution of the bromophenyl compound (0.120 g, 0.35 mmol) in dry tetrahydrofuran (2 ml) at 195 K. After stirring for a further 12 min the reaction mixture was cooled to 173 K, stirred for a further 3 min and then transferred dropwise *via* a double-ended needle into a solution of dry tetrahydrofuran (12 ml) saturated with dry carbon dioxide gas at 173 K. After the addition was complete the reaction mixture was warmed to room temperature, the solvents removed *in vacuo* and the residue partitioned between ice-cold water and dichloromethane (12 ml). Ice-cold aqueous hydrochloric acid (3 M, 3 ml) was added, the organic phase separated, dried (MgSO₄) and evaporated to dryness *in vacuo* to give an oil which slowly crystallized on standing. Recrystallization gave the acetal acid (0.084 g, 79%), m.p. 386–388 K (ether/hexane). (Found: C, 70.9; H, 8.20%. C₁₈H₂₄O₄ requires C, 71.0; H, 7.95%.) Slow diffusion of hexane into an ether solution gave colourless prisms.

Preparation of 2 α -[2,2-bis(4-chlorophenyl)ethoxy]-trans-1-oxadecalin (4). A solution of 2-hydroxy-trans-1-oxadecalin (Chandrasekhar & Kirby, 1983) (156 mg, 1.0 mmol) and *p*-toluenesulphonic acid (one small crystal) in dry benzene (25 ml) was heated under reflux with azeotropic removal of water. After 3 h the benzene was slowly distilled out until the volume of the solution was ca 10 ml. After cooling to 283 K a solution of 2,2-bis(4-chlorophenyl)ethanol (267 mg, 1.0 mmol) in dry dichloromethane (2 ml) was added and the mixture stirred overnight at room temperature. The addition of one more crystal of *p*-toluenesulphonic acid and stirring for a further 6 h completed the reaction. Triethylamine (5 drops) was added and the solvents removed *in vacuo*. Purification by preparative thin-layer chromatography on silica gel gave the axial anomer (4) (247 mg, 61%) as a white solid which could be recrystallized from hexane, m.p. 337–340 K. Slow evaporation of a hexane solution gave colourless plates.

{Values for (4), where differing from those for (3), are given in braces.} Crystal 0.75 × 0.3 × 0.2 {0.55 × 0.5 × 0.25} mm, Stoe-Siemens four-circle diffractometer with monochromated Mo K α radiation, 2 θ _{max} 50°, quadrants $-h + k \pm l$ { $\pm h + k + l$ } and some $+h$ { $-k$ } equivalents, 4574 {4119} profile-fitted intensities (Clegg, 1981). Three check reflections, no significant intensity change. R_{int} 0.025 {0.023} for 2961 {3797} unique reflections, of which 1518 {2237} with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*, written by GMS). Index ranges after merging: h $-8 \rightarrow 8$ { $-21 \rightarrow 21$ }, k $0 \rightarrow 10$, l $0 \rightarrow 30$ { $0 \rightarrow 15$ }.

Cell constants refined from 2 θ values of 35 {40} reflections in range 20–24 {20–23}°. No absorption correction.

Structure solution by routine direct methods. Refinement on F to R 0.066 {0.064}, wR 0.063 {0.055}. All non-H atoms anisotropic; H atoms [except the acidic H of (3), which was refined freely] included using a riding model with C–H 0.96 Å, H–C–H 109.5°, $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. 203 {244} parameters, weighting scheme $w^{-1} = \sigma^2(F) + gF^2$ with g 0.0004 {0.00025}. S 1.80

Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for (3)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
O(1)	1743 (3)	6340 (3)	1950 (1)	76 (1)
C(2)	−118 (5)	6623 (5)	1944 (2)	77 (2)
C(3)	−754 (5)	7709 (4)	1516 (2)	101 (2)
C(4)	−118 (5)	7253 (5)	981 (2)	98 (2)
C(5)	2683 (6)	6546 (5)	500 (2)	96 (2)
C(6)	4641 (6)	6329 (5)	586 (2)	97 (2)
C(7)	5077 (6)	5145 (5)	1010 (2)	87 (2)
C(8)	4297 (5)	5583 (5)	1524 (1)	79 (2)
C(9)	2325 (5)	5855 (4)	1449 (1)	61 (2)
C(10)	1888 (5)	7026 (4)	1030 (2)	73 (2)
O(10)	−1073 (3)	5267 (3)	1869 (1)	73 (1)
C(11)	−843 (6)	4211 (5)	2281 (1)	80 (2)
C(12)	−1338 (5)	2674 (5)	2062 (1)	74 (2)
C(21)	−112 (5)	2135 (4)	1656 (1)	60 (2)
C(22)	1616 (5)	1773 (4)	1803 (1)	70 (2)
C(23)	2777 (5)	1338 (4)	1438 (1)	65 (2)
C(24)	2209 (5)	1236 (3)	903 (1)	54 (1)
C(25)	475 (5)	1586 (4)	756 (1)	67 (2)
C(26)	−678 (5)	2035 (4)	1126 (1)	68 (2)
C(27)	3438 (6)	747 (4)	511 (1)	61 (2)
O(21)	2831 (3)	513 (3)	37 (1)	79 (1)
O(22)	5053 (4)	542 (3)	655 (1)	82 (1)

* Equivalent isotropic U calculated from anisotropic U .

Table 2. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for (4)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Cl(1)	118 (1)	9798 (1)	2926 (1)	90 (1)
Cl(2)	4247 (1)	6282 (2)	9228 (1)	114 (1)
O(1)	2744 (1)	1170 (3)	5767 (2)	63 (1)
C(2)	2032 (2)	819 (4)	5786 (3)	68 (2)
C(3)	2031 (2)	−389 (5)	6561 (4)	92 (2)
C(4)	2564 (2)	−61 (5)	7663 (4)	86 (2)
C(5)	3882 (3)	730 (5)	8649 (4)	98 (2)
C(6)	4621 (2)	1116 (5)	8510 (4)	115 (2)
C(7)	4530 (2)	2341 (5)	7709 (4)	106 (2)
C(8)	3972 (2)	1940 (5)	6641 (4)	81 (2)
C(9)	3247 (2)	1556 (4)	6800 (3)	53 (1)
C(10)	3318 (2)	315 (4)	7590 (3)	65 (2)
O(10)	1681 (1)	2073 (2)	6036 (2)	57 (1)
C(11)	1541 (2)	3236 (4)	5265 (3)	55 (1)
C(12)	1420 (2)	4645 (4)	5832 (3)	47 (1)
C(21)	1085 (1)	5901 (4)	5070 (2)	43 (1)
C(22)	1310 (2)	6250 (4)	4199 (3)	56 (1)
C(23)	1019 (2)	7448 (4)	3541 (3)	58 (1)
C(24)	492 (2)	8278 (4)	3748 (3)	55 (1)
C(25)	238 (2)	7960 (4)	4593 (3)	57 (2)
C(26)	540 (2)	6778 (4)	5249 (3)	50 (1)
C(31)	2130 (2)	5102 (3)	6688 (3)	45 (1)
C(32)	2213 (2)	4898 (4)	7751 (3)	62 (2)
C(33)	2863 (2)	5269 (5)	8541 (3)	73 (2)
C(34)	3426 (2)	5837 (4)	8242 (3)	66 (2)
C(35)	3362 (2)	6031 (4)	7188 (3)	64 (2)
C(36)	2718 (2)	5662 (4)	6424 (3)	55 (1)

* Equivalent isotropic U calculated from anisotropic U .

{1.85}, slope of normal probability plot 1.47 {1.55}. Max. Δ/σ 0.03 {0.02}. Max. and min. heights in final $\Delta\rho$ map +0.24 and -0.20 {+0.23 and -0.32} e Å⁻³. Atomic scattering factors those incorporated in *SHELXTL*.

Discussion. Final atomic coordinates are given in Tables 1 and 2, with derived parameters in Tables 3 and 4.*

The geometry at the acetal centre is almost identical for (3) and (4) (Figs. 1 and 2). Both adopt the usual (+*sc*, +*sc*) conformation about the acetal centre [dihedral angles 67.3 and 65.7 for (3), 67.1 and 64.6° for (4)], and bond lengths are identical within experimental error. In particular, the exocyclic C—OR bond lengths

differ by less than one standard deviation [1.411 (6) for (3), 1.406 (6) Å for (4)]. We took the first of these values as standard for the exocyclic C—OR bond length for an alkyl tetrahydropyranyl acetal (Jones & Kirby, 1984). It should be noted that the mean value of 1.409 Å does not correspond well to the 1.392 Å (for a derivative of an alcohol ROH of p*K_a* 15.5) predicted by extrapolating the original linear relationship derived for a series of aryl tetrahydropyranyl acetals. Every theoretical treatment predicts that the linear relation must hold only over a limited range; we find that we can

Table 4. Bond lengths (Å), bond angles and torsion angles (°) for (4)

C(2)—O(1)	1.416 (6)	C(2)—C(3)	1.491 (8)
C(2)—O(10)	1.406 (6)	C(3)—C(4)	1.519 (7)
C(5)—C(6)	1.533 (8)	C(6)—C(7)	1.496 (8)
C(7)—C(8)	1.520 (7)	C(8)—C(9)	1.517 (7)
C(9)—O(1)	1.441 (5)	C(10)—C(4)	1.523 (7)
C(10)—C(5)	1.519 (6)	C(10)—C(9)	1.502 (6)
C(11)—O(10)	1.423 (5)	C(11)—C(12)	1.526 (6)
C(12)—C(21)	1.513 (5)	C(12)—C(31)	1.528 (5)
C(21)—C(22)	1.384 (6)	C(21)—C(26)	1.392 (6)
C(22)—C(23)	1.386 (6)	C(23)—C(24)	1.357 (6)
C(24)—C(1)	1.751 (4)	C(24)—C(25)	1.380 (7)
C(25)—C(26)	1.378 (6)	C(31)—C(32)	1.370 (6)
C(31)—C(36)	1.382 (6)	C(32)—C(33)	1.393 (6)
C(33)—C(34)	1.365 (7)	C(34)—C(12)	1.747 (5)
C(34)—C(35)	1.366 (7)	C(35)—C(36)	1.368 (5)

Table 3. Bond lengths (Å), bond angles and torsion angles (°) for (3)

C(2)—O(1)	1.428 (6)	C(2)—C(3)	1.504 (7)
C(2)—O(10)	1.411 (6)	C(3)—C(4)	1.519 (7)
C(5)—C(6)	1.493 (7)	C(6)—C(7)	1.522 (7)
C(7)—C(8)	1.513 (7)	C(8)—C(9)	1.509 (6)
C(9)—O(1)	1.434 (5)	C(10)—C(4)	1.527 (7)
C(10)—C(5)	1.563 (7)	C(10)—C(9)	1.506 (6)
C(11)—O(10)	1.404 (6)	C(11)—C(12)	1.513 (7)
C(12)—C(21)	1.506 (6)	C(21)—C(22)	1.371 (6)
C(21)—C(26)	1.380 (6)	C(22)—C(23)	1.370 (6)
C(23)—C(24)	1.394 (6)	C(24)—C(25)	1.374 (6)
C(24)—C(27)	1.469 (6)	C(25)—C(26)	1.378 (6)
C(27)—O(21)	1.270 (5)	C(27)—O(22)	1.263 (6)
C(2)—O(1)—C(9)	113.9 (4)	O(1)—C(2)—C(3)	112.8 (4)
O(1)—C(2)—O(10)	110.2 (4)	C(3)—C(2)—O(10)	108.4 (4)
C(2)—C(3)—C(4)	111.3 (4)	C(3)—C(4)—C(10)	109.6 (4)
C(6)—C(5)—C(10)	110.2 (4)	C(5)—C(6)—C(7)	110.9 (5)
C(6)—C(7)—C(8)	110.4 (4)	C(7)—C(8)—C(9)	111.8 (4)
O(1)—C(9)—C(8)	107.2 (4)	O(1)—C(9)—C(10)	110.2 (4)
C(8)—C(9)—C(10)	111.6 (4)	C(4)—C(10)—C(5)	113.8 (4)
C(4)—C(10)—C(9)	108.5 (4)	C(5)—C(10)—C(9)	109.5 (4)
C(2)—O(10)—C(11)	115.8 (4)	O(10)—C(11)—C(12)	108.6 (4)
C(11)—C(12)—C(21)	112.9 (4)	C(12)—C(21)—C(22)	120.6 (4)
C(12)—C(21)—C(26)	121.1 (4)	C(22)—C(21)—C(26)	118.3 (4)
C(21)—C(22)—C(23)	121.7 (4)	C(22)—C(23)—C(24)	120.0 (4)
C(23)—C(24)—C(25)	118.2 (4)	C(23)—C(24)—C(27)	120.4 (4)
C(25)—C(24)—C(27)	121.4 (4)	C(24)—C(25)—C(26)	121.2 (4)
C(21)—C(26)—C(25)	120.4 (4)	C(24)—C(27)—O(21)	118.7 (5)
C(24)—C(27)—O(22)	119.4 (4)	O(21)—C(27)—O(22)	121.9 (5)
C(9)—O(1)—C(2)—C(3)	-54.0 (5)*	C(9)—O(1)—C(2)—O(10)	67.3 (5)
C(2)—O(1)—C(9)—C(8)	-179.1 (4)	C(2)—O(1)—C(9)—C(10)	59.3 (5)
O(1)—C(2)—C(3)—C(4)	50.3 (5)	O(10)—C(2)—C(3)—C(4)	-72.0 (5)
O(1)—C(2)—O(10)—C(11)	65.7 (5)	C(3)—C(2)—O(10)—C(11)	-170.5 (4)
C(2)—C(3)—C(4)—C(10)	-52.7 (5)	C(3)—C(4)—C(10)—C(5)	179.7 (4)
C(3)—C(4)—C(10)—C(9)	57.5 (5)	C(10)—C(5)—C(6)—C(7)	58.4 (6)
C(6)—C(5)—C(10)—C(4)	-179.2 (4)	C(6)—C(5)—C(10)—C(9)	-57.5 (5)
C(5)—C(6)—C(7)—C(8)	-57.4 (6)	C(6)—C(7)—C(8)—C(9)	55.4 (5)
C(7)—C(8)—C(9)—O(1)	-176.9 (4)	C(7)—C(8)—C(9)—C(10)	-56.1 (5)
O(1)—C(9)—C(10)—C(4)	-60.3 (5)	O(1)—C(9)—C(10)—C(5)	174.9 (4)
C(8)—C(9)—C(10)—C(4)	-179.3 (4)	C(8)—C(9)—C(10)—C(5)	55.9 (5)
C(2)—O(10)—C(11)—C(12)	-158.5 (4)	O(10)—C(11)—C(12)—C(21)	65.3 (5)
C(11)—C(12)—C(21)—C(22)	68.4 (6)	C(11)—C(12)—C(21)—C(26)	-109.7 (5)
C(12)—C(21)—C(22)—C(23)	-177.4 (5)	C(26)—C(21)—C(22)—C(23)	0.8 (7)
C(12)—C(21)—C(26)—C(25)	177.9 (4)	C(22)—C(21)—C(26)—C(25)	-0.3 (6)
C(1)—C(22)—C(23)—C(24)	-0.8 (7)	C(22)—C(23)—C(24)—C(25)	0.2 (6)
C(22)—C(23)—C(24)—C(27)	-179.0 (4)	C(23)—C(24)—C(25)—C(26)	0.4 (6)
C(27)—C(24)—C(25)—C(26)	179.5 (4)	C(23)—C(24)—C(27)—O(21)	172.6 (4)
C(23)—C(24)—C(27)—O(21)	-6.0 (6)	C(25)—C(24)—C(27)—O(21)	-6.5 (6)
C(25)—C(24)—C(27)—O(22)	174.8 (4)	C(24)—C(25)—C(26)—C(21)	-0.3 (6)

* Sign convention as defined by Klyne & Prelog (1960).

C(2)—O(1)—C(9)	113.8 (4)	O(1)—C(2)—C(3)	112.7 (4)
O(1)—C(2)—O(10)	111.4 (4)	C(3)—C(2)—O(10)	108.7 (5)
C(2)—C(3)—C(4)	111.4 (4)	C(3)—C(4)—C(10)	110.7 (5)
C(6)—C(5)—C(10)	111.6 (5)	C(5)—C(6)—C(7)	110.1 (4)
C(6)—C(7)—C(8)	111.7 (5)	C(7)—C(8)—C(9)	109.8 (5)
O(1)—C(9)—C(8)	107.4 (4)	O(1)—C(9)—C(10)	111.2 (4)
C(8)—C(9)—C(10)	112.3 (4)	C(4)—C(10)—C(5)	114.6 (5)
C(4)—C(10)—C(9)	109.3 (4)	C(5)—C(10)—C(9)	109.6 (4)
C(2)—O(10)—C(11)	114.8 (4)	O(10)—C(11)—C(12)	106.6 (4)
C(11)—C(12)—C(21)	113.2 (4)	C(11)—C(12)—C(31)	110.2 (4)
C(21)—C(12)—C(31)	112.5 (4)	C(12)—C(21)—C(22)	122.7 (4)
C(12)—C(21)—C(26)	119.8 (4)	C(22)—C(21)—C(26)	117.5 (4)
C(21)—C(22)—C(23)	121.6 (4)	C(22)—C(23)—C(24)	118.9 (5)
C(1)—C(24)—C(23)	119.5 (4)	C(1)—C(24)—C(25)	118.6 (4)
C(23)—C(24)—C(25)	121.8 (4)	C(24)—C(25)—C(26)	118.6 (4)
C(21)—C(26)—C(25)	121.6 (5)	C(12)—C(31)—C(32)	120.4 (4)
C(12)—C(31)—C(36)	121.8 (4)	C(32)—C(31)—C(36)	117.8 (4)
C(31)—C(32)—C(33)	121.2 (5)	C(32)—C(33)—C(34)	118.9 (5)
C(12)—C(34)—C(35)	119.2 (4)	C(12)—C(34)—C(35)	119.8 (4)
C(33)—C(34)—C(35)	121.0 (4)	C(34)—C(35)—C(36)	119.1 (5)
C(31)—C(36)—C(35)	121.9 (5)		
C(9)—O(1)—C(2)—C(3)	-55.3 (5)*	C(9)—O(1)—C(2)—O(10)	67.1 (5)
C(2)—O(1)—C(9)—C(8)	-178.5 (4)	C(2)—O(1)—C(9)—C(10)	58.3 (5)
O(1)—C(2)—C(3)—C(4)	51.5 (6)	O(10)—C(2)—C(3)—C(4)	-72.4 (5)
O(1)—C(2)—O(10)—C(11)	64.6 (4)	C(3)—C(2)—O(10)—C(11)	-170.7 (4)
C(2)—C(3)—C(4)—C(10)	-51.5 (6)	C(3)—C(4)—C(10)—C(5)	177.4 (4)
C(3)—C(4)—C(10)—C(9)	54.0 (5)	C(10)—C(5)—C(6)—C(7)	56.3 (6)
C(6)—C(5)—C(10)—C(4)	-179.1 (5)	C(6)—C(5)—C(10)—C(9)	-55.9 (6)
C(5)—C(6)—C(7)—C(8)	-56.4 (6)	C(6)—C(7)—C(8)—C(9)	56.5 (6)
C(7)—C(8)—C(9)—O(1)	-179.4 (4)	C(7)—C(8)—C(9)—C(10)	-56.8 (5)
O(1)—C(9)—C(10)—C(4)	-56.7 (5)	O(1)—C(9)—C(10)—C(5)	177.0 (4)
C(8)—C(9)—C(10)—C(4)	-177.0 (4)	C(8)—C(9)—C(10)—C(5)	56.6 (6)
C(2)—O(10)—C(11)—C(12)	-160.5 (3)	O(10)—C(11)—C(12)—C(21)	-166.0 (3)
O(10)—C(11)—C(12)—C(31)	67.0 (4)	C(11)—C(12)—C(21)—C(22)	-43.0 (5)
C(11)—C(12)—C(21)—C(26)	138.5 (4)	C(11)—C(12)—C(21)—C(32)	82.8 (5)
C(31)—C(12)—C(21)—C(26)	-95.7 (5)	C(11)—C(12)—C(31)—C(32)	-106.3 (5)
C(11)—C(12)—C(31)—C(36)	70.5 (5)	C(21)—C(12)—C(31)—C(32)	126.3 (5)
C(21)—C(12)—C(31)—C(36)	-56.9 (5)	C(12)—C(21)—C(22)—C(23)	-177.0 (4)
C(2)—C(21)—C(22)—C(23)	1.5 (6)	C(12)—C(21)—C(26)—C(25)	177.9 (4)
C(22)—C(21)—C(26)—C(25)	-0.6 (6)	C(21)—C(22)—C(23)—C(24)	1.1 (6)
C(22)—C(23)—C(24)—C(1)	179.9 (3)	C(22)—C(23)—C(24)—C(25)	-0.2 (6)
C(1)—C(24)—C(25)—C(26)	-179.0 (3)	C(23)—C(24)—C(25)—C(26)	1.1 (6)
C(24)—C(25)—C(26)—C(21)	-0.7 (6)	C(12)—C(31)—C(32)—C(33)	178.2 (4)
C(36)—C(31)—C(32)—C(33)	1.3 (6)	C(12)—C(31)—C(36)—C(35)	-178.1 (4)
C(32)—C(31)—C(36)—C(35)	-1.2 (6)	C(31)—C(32)—C(33)—C(34)	-0.4 (7)
C(32)—C(33)—C(34)—C(12)	-179.2 (4)	C(32)—C(33)—C(34)—C(35)	-0.5 (7)
C(12)—C(34)—C(35)—C(36)	179.2 (4)	C(33)—C(34)—C(35)—C(36)	0.6 (7)
C(34)—C(35)—C(36)—C(31)	0.3 (6)		

* Sign convention as defined by Klyne & Prelog (1960).

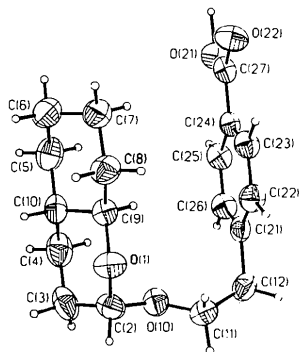


Fig. 1. Thermal ellipsoid plot of (3) (35% level), showing the atom-numbering scheme.

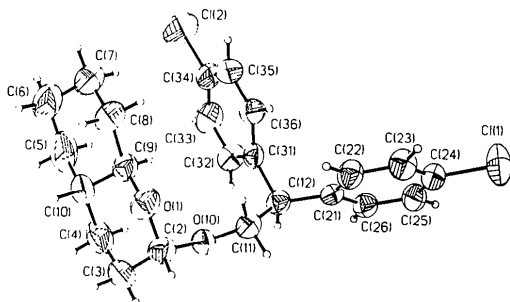


Fig. 2. Thermal ellipsoid plot of (4) (50% level), showing the atom-numbering scheme.

fit the complete set of data satisfactorily to the Morse function, which turns out to have a substantial linear region for moderate values of $(r - r_0)$ (for details see Jones & Kirby, 1984).

It is noteworthy that the exocyclic C—OR bonds are significantly shorter than the endocyclic C—O bonds at the acetal centre [1.428 (6) and 1.416 (6) Å respectively for (3) and (4)], as predicted by the linear relationships between bond length and reactivity discussed previously (Briggs, Glenn, Jones, Kirby &

Ramaswamy, 1984). The two acetal oxygen atoms might be expected to have similar effective electronegativities, giving rise to equal C—O bond lengths at the acetal centre. In practice the ring oxygen behaves as though it is slightly *more* electronegative. This is presumably a result of constraints imposed by the ring structure, perhaps on bond angles at the acetal centre, or at the ring oxygen (Deslongchamps, 1983). In fact the only systematic difference apparent between the angles in the cyclic series (1–4) and a similar acyclic series methoxymethyl acetals (MeOCH₂OR; Jones, Sheldrick, Kirby & Briggs, 1985) is the angle at the acetal carbon, which may be smaller ($110.3 \pm 1.9^\circ$ for six compounds) for the cyclic acetals. For the methoxymethyl series MeOCH₂OR is $112.7 \pm 0.4^\circ$ for four compounds.

The molecules of (3) pack so as to allow the formation of carboxylic acid dimers, with O(22)···O(21) 2.62 (1) Å (second atom at $1 - x, -y, -z$). (4) shows no unusually short intermolecular contacts.

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[Ph₄As][Cl₂OW(μ-Cl){μ-S(p-C₆H₄CH₃)}₂WOCl₂] and Co[(C₁₂H₁₀OP)₂Pt(C₃H₁₀NS₂)₂].2CHCl₃: corrigenda.* By RICHARD E. MARSH, *Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, USA*

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Abstract

Both tetraphenylarsonium μ -chloro-bis-(μ -*p*-tolylthiolato)-bis-[dichlorooxotungstate(V)] and bis[*N,N'*-diethylthiocarbam-