

Equatorial 2-Phenoxy-*trans*-1-oxadecalin

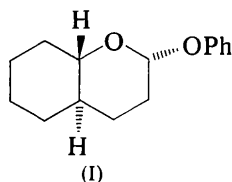
BY PETER G. JONES,\* OLGA KENNARD,†  
SOSALE CHANDRASEKHAR AND ANTHONY J. KIRBY

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

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**Abstract.** C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>,  $M_r = 232.23$ , triclinic,  $P\bar{1}$ ,  $a = 5.475(2)$ ,  $b = 11.437(4)$ ,  $c = 11.467(4)$  Å,  $\alpha = 115.72(2)$ ,  $\beta = 94.67(2)$ ,  $\gamma = 95.26(2)^\circ$ ,  $U = 638.3$  Å<sup>3</sup>,  $D_x = 1.209$  Mg m<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 0.54$  mm<sup>-1</sup>. The structure was refined to  $R = 0.051$  for 1668 unique reflexions. The two C–O lengths of the acetal group in this equatorial isomer do not differ significantly, whereas in the corresponding axial isomer they differ by 0.028 Å.

**Introduction.** Continuing our systematic examination of the effects of ground-state structure on the reactivity of acetals (Jones, Kennard, Kirby & Osborne, 1978; Jones, Kennard, Kirby, Osborne & Malik, 1978; Jones, Kennard, Chandrasekhar & Kirby, 1978) we report the crystal structure of the conformationally locked acetal (I), which possesses an equatorial leaving group. We recently reported the structure of the isomer of (I) with the phenoxy group axial, and thus antiperiplanar to one of the lone-pair orbitals on the ring O atom (Jones, Kennard, Chandrasekhar & Kirby, 1978). The interaction between this lone pair and the exocyclic C–O bond may control the reactivity of this acetal (Chandrasekhar & Kirby, 1978) and we are looking for evidence of such an interaction in the ground states of compounds of this sort.



Large colourless crystals were obtained from methylene dichloride/petroleum spirit; crystals were sealed in glass capillaries since they are slowly attacked by atmospheric moisture. Intensities were measured on a Philips PW 1100 diffractometer with graphite-monochromated Cu  $K\alpha$  radiation, and a crystal  $0.7 \times 0.4 \times$

0.2 mm. Cell dimensions were obtained by a least-squares method from 25 strong reflexions. 2523 reflexions were measured in the range  $3^\circ < 2\theta < 120^\circ$ , giving 1673 unique reflexions with  $F > 4\sigma(F)$  after application of Lp corrections and averaging of equivalent reflexions.

Attempts to solve the structure with *SHELX* (G. M. Sheldrick) were unsuccessful, generating only *E* maps with repeating six-membered rings. The program *XCSD*, which incorporates a pseudotangent refinement to select the starting set (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973) and the negative quartet test NQEST (De Titta, Edmonds, Langs & Hauptman, 1975), gave positions for all non-hydrogen atoms. Figures of merit were NQEST  $-0.964$ ,  $RA$  (a point atom  $R$  factor based on observed peaks) 0.194,  $R\alpha$  (Roberts *et al.*, 1973) 0.064. Least-squares refinement (all atoms anisotropic) proceeded to  $R = 0.12$ ; a difference synthesis then showed all H atoms. In the final stages of refinement all C–H lengths and H–C–H angles were fixed at 1.08 Å and  $109.5^\circ$  respectively; H atoms were allotted an overall isotropic temperature factor and five reflexions clearly in error were omitted. The final  $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o|$  was 0.067, with a corresponding  $R$  of 0.051. The weighting scheme was  $w = 1/[\sigma^2(F) + 0.0015F^2]$ . A final difference map showed no peaks  $>0.19$  e Å<sup>-3</sup>.

Final atomic coordinates are given in Table 1, with derived bond lengths and angles in Table 2 and torsion angles in Table 3.‡ Diagrams of the structure are given in Figs. 1 and 2.

**Discussion.** A comparison of the structures of the axial (Jones, Kennard, Chandrasekhar & Kirby, 1978) and equatorial (I) isomers of 2-phenoxy-*trans*-1-oxadecalin reveals significant differences in the structure of the acetal group, which are relevant to the ease of the C–O cleavage reaction. The angle O(1)–C(2)–O(10) is

\* Present address: Anorganisch-Chemisches Institut der Universität Göttingen, Tammannstrasse 4, 3400 Göttingen-Weende, Federal Republic of Germany.

† External Staff, Medical Research Council.

‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33871 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* ( $\times 10^4$ )Overall isotropic temperature factor for H atoms: 0.075 (1) Å<sup>2</sup>.

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	-70 (2)	8932 (1)	2634 (1)
C(2)	-125 (3)	8952 (1)	1411 (1)
C(3)	-510 (3)	7582 (2)	303 (1)
C(4)	1590 (3)	6868 (2)	499 (2)
C(5)	4011 (4)	6333 (2)	2163 (2)
C(6)	4155 (4)	6432 (2)	3528 (2)
C(7)	4222 (3)	7839 (2)	4559 (2)
C(8)	2045 (3)	8447 (2)	4246 (2)
C(9)	1998 (3)	8350 (1)	2889 (1)
C(10)	1812 (3)	6925 (1)	1858 (2)
O(10)	-2147 (2)	9594 (1)	1283 (1)
C(11)	-1843 (3)	10949 (1)	1972 (1)
C(12)	-3730 (3)	11543 (2)	1687 (2)
C(13)	-3580 (3)	12897 (2)	2307 (2)
C(14)	-1532 (4)	13649 (2)	3197 (2)
C(15)	343 (3)	13045 (2)	3473 (2)
C(16)	195 (3)	11695 (2)	2877 (2)
H(21)	1616	9447	1366
H(31)	-2262	7067	304
H(32)	-495	7630	-617
H(41)	1230	5856	-225
H(42)	3308	7326	383
H(51)	5692	6852	2085
H(52)	3827	5314	1465
H(61)	2553	5839	3579
H(62)	5813	6067	3725
H(71)	4133	7845	5499
H(72)	5931	8409	4589
H(81)	2231	9466	4947
H(82)	338	7933	4305
H(91)	3706	8865	2834
H(101)	165	6340	1878
H(121)	-5318	10955	983
H(131)	-5063	13366	2096
H(141)	-1402	14705	3673
H(151)	1945	13634	4163
H(161)	1653	11228	3115

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

C(2)–O(1)	1.411 (3)	C(2)–C(3)	1.511 (4)
C(2)–O(10)	1.415 (3)	C(3)–C(4)	1.526 (5)
C(4)–C(10)	1.526 (5)	C(5)–C(6)	1.515 (5)
C(5)–C(10)	1.522 (5)	C(6)–C(7)	1.523 (4)
C(7)–C(8)	1.527 (5)	C(8)–C(9)	1.510 (5)
C(9)–O(1)	1.437 (3)	C(9)–C(10)	1.530 (4)
C(11)–O(10)	1.386 (3)	C(11)–C(12)	1.379 (4)
C(11)–C(16)	1.385 (3)	C(12)–C(13)	1.387 (3)
C(13)–C(14)	1.383 (3)	C(14)–C(15)	1.378 (4)
C(15)–C(16)	1.382 (3)		
C(2)–O(1)–C(9)	111.4 (2)	O(1)–C(2)–C(3)	111.5 (2)
O(1)–C(2)–O(10)	107.0 (2)	C(3)–C(2)–O(10)	108.8 (2)
C(2)–C(3)–C(4)	108.4 (2)	C(3)–C(4)–C(10)	111.1 (2)
C(6)–C(5)–C(10)	111.5 (3)	C(5)–C(6)–C(7)	111.9 (3)
C(6)–C(7)–C(8)	111.0 (2)	C(7)–C(8)–C(9)	110.4 (2)
O(1)–C(9)–C(8)	108.6 (2)	O(1)–C(9)–C(10)	110.3 (2)
C(8)–C(9)–C(10)	111.4 (2)	C(4)–C(10)–C(5)	113.8 (2)
C(4)–C(10)–C(9)	109.6 (2)	C(5)–C(10)–C(9)	109.0 (2)
C(2)–O(10)–C(11)	117.4 (2)	O(10)–C(11)–C(12)	115.3 (2)
O(10)–C(11)–C(16)	124.2 (3)	C(12)–C(11)–C(16)	120.5 (2)
C(11)–C(12)–C(13)	119.7 (2)	C(12)–C(13)–C(14)	120.1 (3)
C(13)–C(14)–C(15)	119.7 (3)	C(14)–C(15)–C(16)	120.8 (2)
C(11)–C(16)–C(15)	119.2 (3)		

107.0° in (I), compared with 110.9° in its axial isomer. Similar differences are observed between many axial and equatorial glycosides, and have been discussed by Gorenstein & Kar (1977). This angle must open to 120° in the oxocarbenium ion intermediates formed on C–O cleavage, and evidently the isomer with the leaving group axial (and thus antiperiplanar to a lone pair on the O atom) is closer in geometry to this intermediate, and thus to the transition state leading to it.

Differences in bond lengths are consistent with this interpretation. The two C–O lengths of the acetal group do not differ significantly in the equatorial isomer [C(2)–O(1) = 1.411 (3), C(2)–O(10) =

Table 3. *Selected torsion angles* (°)

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

C(9)–O(1)–C(2)–C(3)	63.9 (2)
C(9)–O(1)–C(2)–O(10)	-177.4 (2)
C(2)–O(1)–C(9)–C(8)	176.1 (2)
C(2)–O(1)–C(9)–C(10)	-61.5 (3)
O(1)–C(2)–C(3)–C(4)	-58.6 (3)
O(10)–C(2)–C(3)–C(4)	-176.3 (2)
O(1)–C(2)–O(10)–C(11)	76.8 (3)
C(3)–C(2)–O(10)–C(11)	-162.7 (2)
C(2)–C(3)–C(4)–C(10)	53.4 (3)
C(3)–C(4)–C(10)–C(5)	-175.0 (2)
C(3)–C(4)–C(10)–C(9)	-52.7 (3)
C(10)–C(5)–C(6)–C(7)	-55.3 (3)
C(6)–C(5)–C(10)–C(4)	179.3 (2)
C(6)–C(5)–C(10)–C(9)	56.6 (3)
C(5)–C(6)–C(7)–C(8)	53.9 (3)
C(6)–C(7)–C(8)–C(9)	-55.1 (3)
C(7)–C(8)–C(9)–O(1)	-180.0 (2)
C(7)–C(8)–C(9)–C(10)	58.3 (3)
O(1)–C(9)–C(10)–C(4)	55.4 (3)
O(1)–C(9)–C(10)–C(5)	-179.4 (2)
C(8)–C(9)–C(10)–C(4)	176.1 (2)
C(8)–C(9)–C(10)–C(5)	-58.7 (3)
C(2)–O(10)–C(11)–C(12)	171.9 (3)
C(2)–O(10)–C(11)–C(16)	-7.2 (3)
O(10)–C(11)–C(12)–C(13)	-178.8 (3)
O(10)–C(11)–C(16)–C(15)	177.7 (3)

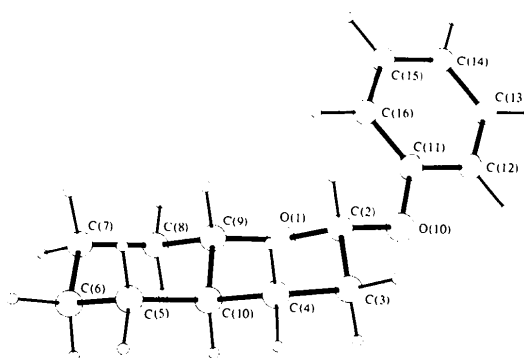


Fig. 1. The title compound showing the labelling scheme for non-hydrogen atoms. H atoms are numbered such that H(*mn*) is the *n*th H on C(*m*).

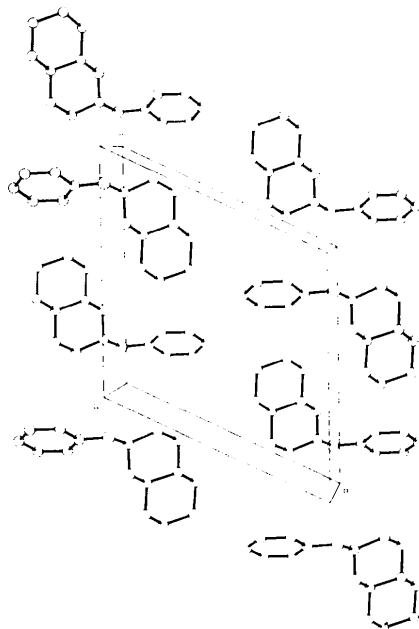


Fig. 2. Packing diagram viewed down  $a^*$  (H atoms omitted).

1.415 (3) Å], whereas the corresponding lengths in the axial isomer are 1.405 and 1.433 Å. The shortening of the C(2)—O(1) bond (which becomes a partial double bond in the transition state for C—O cleavage) is not significant in this latter compound, but the C(2)—O(10)

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## [1,1-Bis(1-phenylethylidenoxy)ethyl]benzol

VON ALFRED GIEREN UND VIKTOR LAMM

*Max-Planck-Institut für Biochemie, Abteilung für Strukturforchung I, 8033 Martinsried bei München, Bundesrepublik Deutschland*

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**Abstract.**  $C_{24}H_{24}N_2O_2$ ,  $M_r = 372.5$ , monoclinic,  $B2$ ,  $a = 20.253$  (3),  $b = 12.981$  (2),  $c = 8.253$  (5) Å,  $\gamma = 104.90$  (4)°,  $V = 2096.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.180$ ,  $D_m = 1.188$  Mg m<sup>-3</sup>. The structure analysis was carried out with a crystal twinned on (100). It is shown that one of the products of the transition-metal-catalyzed self-condensation of benzophenone oxime is an acetal of acetophenone with acetophenone oxime.

**Einleitung.** Kürzlich wurde über die Struktur eines Produktes der übergangsmetallkatalysierten Selbstkondensation von *syn*-Benzaldoxim berichtet (Gieren &

bond is clearly lengthened. We are now examining related compounds with better leaving groups, where larger differences are to be expected.

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Dederer, 1977; Gieren, Dederer, Ugi & Stüber, 1977). In einer analogen Reaktion setzte Stüber (1977) anstelle von *syn*-Benzaldoxim Acetophenoxim (I) um. Zwei der bei der Reaktion erhaltenen Produkte (II, III) haben wir untersucht. Im Gegensatz zu den ursprünglichen Strukturvorstellungen (Stüber, 1977) konnten wir eines dieser Produkte (II) über eine Einkristallröntgenstrukturanalyse als [1,1-Bis(1-phenylethylidenoxy)ethyl]benzol ( $C_{24}H_{24}N_2O_2$ ), d.h. als ein Acetal von Acetophenon mit Acetophenoxim identifizieren. In dem Produkt (II) wiesen wir über ein <sup>1</sup>H-NMR-Spektrum als Verunreinigung