

Bond Length and Reactivity. The Pinacol Rearrangement. 2.* Structure of *trans*-2-Phenoxy-cyclohexanol

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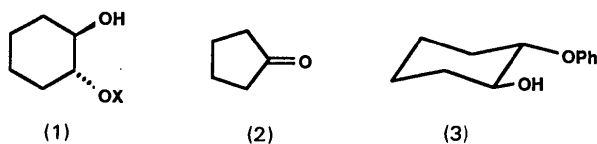
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Abstract. C₁₂H₁₆O₂, *M_r* = 192.26, monoclinic, *P*2₁/*c*, *a* = 5.420 (2), *b* = 20.634 (5), *c* = 19.136 (4) Å, β = 93.45 (2)°, *V* = 2136 Å³, *Z* = 8, *D_x* = 1.195 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 0.075 mm⁻¹, *F*(000) = 832, *T* = 293 K. The structure was refined to *R* = 0.064 for 2049 unique observed reflections. The two molecules in the asymmetric unit are closely similar: the orientations of the phenyl ring differ by *ca* 12°. The C–O(Ph) bond lengths are 1.437 (5) and 1.442 (5) Å, compared with 1.428 (5) and 1.427 (5) Å for the C–O(H) bonds and with 1.429 (2) Å in the parent diol. Hydrogen bonds connect the two independent molecules to each other and also link the pairs thus formed in columns parallel to the short *a* axis.

Introduction. We have prepared a series of unsymmetrical derivatives of *trans*-cyclohexane-1,2-diol (1), hoping that by making OX a better leaving group we may be able to induce changes in geometry recognizable as the initial stages of the pinacol rearrangement (1)→(2). In our previous paper we reported the structure of the parent diol [(1), X = H]. We now describe the monophenyl ether (3).



Experimental. The ether (3) was prepared by the reaction of sodium phenoxide with cyclohexane oxide. Evaporation of a solution in petrol–dichloromethane gave colourless rectangular blocks, m.p. 353–355 K. A fragment *ca* 0.65 × 0.35 × 0.3 mm was cut from a crystal several mm long and mounted in a glass

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> *
C(11)	9651 (5)	2439 (1)	1739 (1)	40 (1)
C(12)	10133 (6)	2800 (1)	1068 (1)	40 (1)
C(13)	12311 (6)	2503 (1)	727 (2)	49 (1)
C(14)	11942 (7)	1782 (2)	585 (2)	56 (1)
C(15)	11418 (6)	1425 (2)	1256 (2)	56 (1)
C(16)	9206 (6)	1727 (1)	1592 (2)	51 (1)
O(1)	7544 (4)	2743 (1)	2022 (1)	47 (1)
O(2)	10718 (4)	3463 (1)	1212 (1)	59 (1)
C(21)	7265 (5)	2708 (1)	2727 (1)	39 (1)
C(22)	5291 (6)	3058 (1)	2962 (2)	45 (1)
C(23)	4846 (6)	3059 (2)	3665 (2)	57 (1)
C(24)	6379 (7)	2717 (2)	4137 (2)	57 (1)
C(25)	8323 (6)	2379 (2)	3905 (2)	54 (1)
C(26)	8780 (6)	2370 (2)	3201 (2)	50 (1)
C(11')	4837 (6)	5035 (1)	1839 (2)	42 (1)
C(12')	5256 (6)	4709 (1)	1150 (1)	40 (1)
C(13')	7449 (6)	5010 (1)	820 (2)	52 (1)
C(14')	7167 (7)	5742 (2)	728 (2)	61 (1)
C(15')	6659 (6)	6060 (2)	1421 (2)	61 (1)
C(16')	4438 (6)	5756 (1)	1737 (2)	52 (1)
O(1')	2692 (4)	4729 (1)	2105 (1)	48 (1)
O(2')	5765 (4)	4034 (1)	1240 (1)	56 (1)
C(21')	2401 (6)	4723 (1)	2811 (1)	42 (1)
C(22')	421 (6)	4361 (2)	3021 (2)	50 (1)
C(23')	-26 (7)	4317 (2)	3717 (2)	67 (2)
C(24')	1500 (8)	4630 (2)	4214 (2)	67 (2)
C(25')	3446 (7)	4986 (2)	4005 (2)	66 (2)
C(26')	3929 (6)	5040 (2)	3306 (2)	54 (1)

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

capillary. 4802 profile-fitted intensities (Clegg, 1981) were measured on a Stoe–Siemens four-circle diffractometer using monochromated Mo *K*α radiation ($2\theta_{\text{max}} = 50^\circ$). Three check reflections showed no significant intensity change. Merging equivalents gave 3771 unique reflections (*R*_{int} = 0.029; index ranges after merging *h* –6 to 6, *k* 0 to 24, *l* 0 to 22), of which 2049 with *F* > 4σ(*F*) were used for all calculations *via* program system *SHELXTL* (Sheldrick, 1986). Cell constants were refined from 2θ values of 40 reflections in the range 20–23°.

The structure was solved by routine direct methods and subjected to cascade least-squares refinement on *F*.

* Part 1: Jones, Edwards & Kirby (1989).

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Table 2. Bond lengths (Å), bond angles (°) and selected torsion angles (°)

	Mol. 1	Mol. 2		Mol. 1	Mol. 2
C(11)–C(12)	1.520 (5)	1.509 (5)	C(11)–C(16)	1.513 (5)	1.515 (5)
C(11)–O(1)	1.437 (5)	1.442 (5)	C(12)–C(13)	1.513 (6)	1.513 (6)
C(12)–O(2)	1.428 (5)	1.427 (5)	C(13)–C(14)	1.523 (6)	1.526 (6)
C(14)–C(15)	1.522 (6)	1.519 (6)	C(15)–C(16)	1.526 (6)	1.515 (6)
C(21)–O(1)	1.368 (5)	1.370 (5)	C(21)–C(22)	1.388 (5)	1.387 (6)
C(21)–C(26)	1.377 (5)	1.383 (5)	C(22)–C(23)	1.380 (6)	1.371 (6)
C(23)–C(24)	1.383 (6)	1.383 (6)	C(24)–C(25)	1.361 (6)	1.364 (7)
C(25)–C(26)	1.384 (6)	1.385 (6)	O(2)–H(O2)	0.84 (4)	0.91 (4)
C(12)–C(11)–C(16)	110.7 (3)	110.7 (4)	C(12)–C(11)–O(1)	106.6 (3)	106.3 (3)
C(16)–C(11)–O(1)	111.9 (3)	111.3 (4)	C(11)–C(12)–C(13)	110.1 (3)	110.1 (3)
C(11)–C(12)–O(2)	110.7 (3)	111.6 (3)	C(13)–C(12)–O(2)	107.6 (3)	107.5 (3)
C(12)–C(13)–C(14)	112.1 (4)	112.3 (4)	C(13)–C(14)–C(15)	110.5 (4)	110.4 (4)
C(14)–C(15)–C(16)	110.5 (4)	111.1 (4)	C(11)–C(16)–C(15)	110.7 (4)	110.3 (4)
C(11)–O(1)–C(21)	119.1 (3)	119.7 (3)	O(1)–C(21)–C(22)	115.3 (4)	115.3 (4)
O(1)–C(21)–C(26)	125.4 (4)	124.8 (4)	C(22)–C(21)–C(26)	119.3 (4)	119.9 (4)
C(21)–C(22)–C(23)	120.1 (4)	120.1 (4)	C(22)–C(23)–C(24)	120.1 (4)	120.3 (5)
C(23)–C(24)–C(25)	119.6 (4)	119.3 (5)	C(24)–C(25)–C(26)	120.8 (4)	121.4 (4)
C(21)–C(26)–C(25)	120.0 (4)	118.9 (4)			
C(16)–C(11)–C(12)–C(13)	–57.2 (4)	57.6 (4)	C(16)–C(11)–C(12)–O(2)	–176.1 (3)	176.9 (3)
O(1)–C(11)–C(12)–C(13)	–179.1 (3)	178.6 (3)	O(1)–C(11)–C(12)–O(2)	62.1 (4)	–62.1 (4)
C(12)–C(11)–C(16)–C(15)	58.3 (4)	–58.9 (4)	O(1)–C(11)–C(16)–C(15)	176.9 (3)	–176.9 (3)
C(12)–C(11)–O(1)–C(21)	–154.2 (3)	154.2 (3)	C(16)–C(11)–O(1)–C(21)	84.7 (4)	–85.1 (4)
C(11)–C(12)–C(13)–C(14)	56.2 (4)	–55.7 (4)	O(2)–C(12)–C(13)–C(14)	176.9 (3)	–177.4 (3)
C(12)–C(13)–C(14)–C(15)	–55.6 (5)	54.2 (5)	C(13)–C(14)–C(15)–C(16)	55.4 (5)	–54.8 (5)
C(14)–C(15)–C(16)–C(11)	–57.4 (4)	57.6 (4)	C(11)–O(1)–C(21)–C(22)	175.1 (4)	–173.6 (4)
C(11)–O(1)–C(21)–C(26)	–3.9 (5)	5.7 (5)			

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

All non-H atoms were refined anisotropically, C–H using a riding model, O–H with fixed *U* but otherwise freely. The final *R* value was 0.064, with *wR* = 0.058. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003 F^2$. 259 parameters; *S* = 1.6; max. Δ/σ = 0.03, max. $\Delta\rho$ within $\pm 0.2 e \text{ \AA}^{-3}$. Scattering factors from the *SHELXTL* program.

Discussion. Final atomic coordinates and derived parameters are given in Tables 1 and 2.* Thermal ellipsoid plots of the two independent molecules of (3) are shown in Fig. 1. The two molecules differ by *ca* 12° in the orientation of the phenyl rings, but are otherwise very similar (Table 2). They are linked by a hydrogen bond, with O(2')...O(2) 2.935 (6), O(2')...H(O2) 2.12 (4) Å, O–H...O 166 (3)°. A further hydrogen bond, O(2')...O(2) 2.975 (6), H(O2')...O(2) 2.14 (4) Å, O–H...O 153 (3)°, with the second atoms at $-1+x, y, z$, results in infinite hydrogen-bonded columns of molecules parallel to *a* (see Figs. 1 and 2).

The largest structural change on introducing the phenyl ether group into the diol is the marginal increase in length of the C(1)–OPh bond, which is 1.437 (5) and 1.442 (5) Å in (3), compared with 1.429 (2) Å in (1), *X* = H. The puckering of the ring is also increased slightly, with the largest ring torsion angle 58.3 (58.9)°

* 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 51416 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

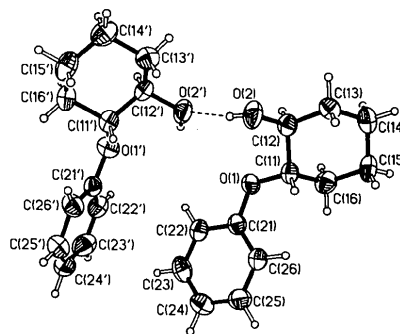


Fig. 1. Molecular structure of (3), showing the atom-numbering scheme.

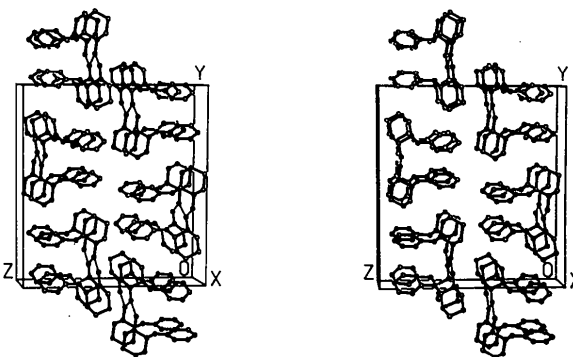


Fig. 2. Molecular packing diagram, showing the intermolecular pattern of hydrogen bonding.

about C(11)—C(16), involving the substituted centre. Note that the conformations about the ring C—O bonds indicate that C(11)—O(1) and C(12)—O(2) correspond to C(2)—O(2) and C(1)—O(1), respectively, in the parent diol (Jones, Edwards & Kirby, 1989). The comparisons show negligible changes in bond and torsion angles across the O—C—O system, though the H bonds are significantly longer than in the diol (2.94, 2.98 Å compared with 2.73, 2.78 Å). Presumably the lattice has to relax to accommodate the aromatic ring.

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Bond Length and Reactivity. The Pinacol Rearrangement. 3.* Structures of *trans*-2-Hydroxycyclohexyl 4-Nitrobenzoate and 2,4-Dinitrobenzoate Esters

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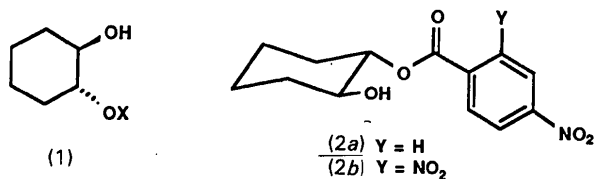
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Abstract. The 4-nitrobenzoate ester (2a): C₁₃H₁₅NO₅, $M_r = 265.26$, triclinic, $P\bar{1}$, $a = 5.659$ (2), $b = 8.167$ (2), $c = 14.167$ (4) Å, $\alpha = 91.94$ (3), $\beta = 101.37$ (2), $\gamma = 90.81$ (2)°, $V = 641.4$ Å³, $Z = 2$, $D_x = 1.37$ Mg m⁻³, $F(000) = 280$, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 0.1$ mm⁻¹, $T = 293$ K. The structure was refined to $R = 0.045$ for 2215 unique observed reflections. The ester C—OX bond length is 1.466 (3) Å. The molecules are linked parallel to the a axis by hydrogen bonds between the hydroxyl group and the carbonyl oxygen. The 2,4-dinitrobenzoate ester (2b): C₁₃H₁₄N₂O₇, $M_r = 310.26$, triclinic, $P\bar{1}$, $a = 7.562$ (2), $b = 8.352$ (2), $c = 12.790$ (2) Å, $\alpha = 91.73$ (2), $\beta = 100.83$ (2), $\gamma = 116.33$ (1)°, $V = 705.2$ Å³, $Z = 2$, $D_x = 1.46$ Mg m⁻³, $F(000) = 324$, $\mu = 0.11$ mm⁻¹, $T = 293$ K. The structure was refined to $R = 0.046$ for 2327 unique observed reflections. The ester C—OX bond length is 1.473 (3) Å. The molecules are linked in head-to-tail pairs by hydrogen bonds between the hydroxyl group and an oxygen atom of a nitro group.

Introduction. This is the third of a short series of papers on the crystal structures of *trans*-1,2-cyclohexanediol and selected monoalkylated and acylated derivatives (1), of potential interest in connection with the detailed mechanism of the pinacol rearrangement. We have reported structures for the parent diol [(1), $X = \text{H}$] and its monophenyl ether [(1), $X = \text{Ph}$] (Jones, Edwards & Kirby, 1989*a,b*). This paper deals with two monoesters, the 4-nitrobenzoate (2a) and the 2,4-dinitrobenzoate (2b).



Experimental. The 4-nitrobenzoate (2a) was prepared by acylating the diol with the acid chloride in the presence of pyridine. Diffusion of petrol into a solution in dichloromethane gave colourless or pale yellow blocks, m.p. 369–370 K [lit. (Loibner & Zbiral, 1976): 364–368 K]. The dinitrobenzoate (2b) was obtained from the diol and 2,4-dinitrobenzoic acid in Et₂O/tetrahydrofuran, using dicyclohexyl carbodiimide as

* Part 2: Jones, Edwards & Kirby (1989*b*).

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