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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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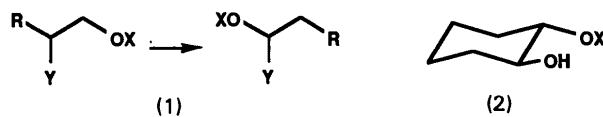
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Abstract. C₆H₁₂O₂, *M_r* = 116.16, orthorhombic, *Pbca*, *a* = 7.8884 (6), *b* = 19.332 (2), *c* = 8.5009 (8) Å, *V* = 1296.4 Å³, *Z* = 8, *D_x* = 1.19 Mg m⁻³, *F*(000) = 512, λ(Mo *K*α) = 0.71069 Å, μ = 0.08 mm⁻¹, *T* = 293 K. The structure was refined 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].



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

* Previous paper: Jones, Kirby & Ryder (1989).

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

	x	y	z	U_{eq}^*
C(1)	1650 (1)	1022 (1)	4417 (1)	35 (1)
C(2)	2852 (1)	593 (1)	5288 (1)	35 (1)
C(3)	3898 (2)	1024 (1)	6496 (2)	48 (1)
C(4)	4731 (2)	1649 (1)	5731 (2)	56 (1)
C(5)	3433 (2)	2085 (1)	4864 (2)	58 (1)
C(6)	2471 (2)	1650 (1)	3664 (1)	44 (1)
O(1)	853 (1)	630 (1)	3199 (1)	41 (1)
O(2)	2093 (1)	22 (1)	5997 (1)	52 (1)

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

Table 2. Bond lengths (\AA), bond angles ($^\circ$) and torsion angles ($^\circ$)

C(1)–C(2)	1.514 (3)	C(1)–C(6)	1.517 (3)
C(1)–O(1)	1.429 (2)	C(2)–C(3)	1.518 (3)
C(2)–O(2)	1.429 (2)	C(3)–C(4)	1.522 (3)
C(4)–C(5)	1.517 (3)	C(5)–C(6)	1.524 (3)
O(1)–H(11)	0.82 (2)	O(2)–H(21)	0.76 (2)
C(2)–C(1)–C(6)	110.8 (2)	C(2)–C(1)–O(1)	111.3 (2)
C(6)–C(1)–O(1)	107.8 (2)	C(1)–C(2)–C(3)	111.3 (2)
C(1)–C(2)–O(2)	107.9 (2)	C(3)–C(2)–O(2)	111.8 (2)
C(2)–C(3)–C(4)	111.1 (2)	C(3)–C(4)–C(5)	110.9 (2)
C(4)–C(5)–C(6)	110.8 (2)	C(1)–C(6)–C(5)	111.8 (2)
C(1)–O(1)–H(11)	108 (1)	C(2)–O(2)–H(21)	110 (1)
C(6)–C(1)–C(2)–C(3)	55.6 (2)	C(6)–C(1)–C(2)–O(2)	178.7 (2)
O(1)–C(1)–C(2)–C(3)	175.5 (2)	O(1)–C(1)–C(2)–O(2)	–61.4 (2)
C(2)–C(1)–C(6)–C(5)	–55.2 (2)	O(1)–C(1)–C(6)–C(5)	–177.2 (2)
C(1)–C(2)–C(3)–C(4)	–56.4 (2)	O(2)–C(2)–C(3)–C(4)	–177.2 (2)
C(2)–C(3)–C(4)–C(5)	56.3 (3)	C(3)–C(4)–C(5)–C(6)	–55.6 (3)
C(4)–C(5)–C(6)–C(1)	55.4 (3)		

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

the parent compound (2), $X = H$. Preliminary crystallographic data (cell constants *etc.*) for this compound were published by White (1931). It also appears in a molecular complex with *N*-methylmorpholine *N*-oxide in a structure described by Chanzy, Maia & Pérez (1982). The uncomplexed structure was then determined by Sillanpää, Leskelä & Hiltunen (1984; hereafter SLH). However, we were not satisfied with their results for several reasons: (i) they report considerable crystal decay (35–38% based on check reflections); (ii) their reflection data/parameter ratio was very poor (499/122); and (iii) e.s.d.'s on their bond lengths were rather higher (typically 0.004–0.005 \AA) than we need for very detailed comparisons of the parent compound with other members of the series. We therefore redetermined the structure. The results are reported below, and used as a basis for discussion in the following three papers.

Experimental. The commercially available diol was crystallized by diffusing pentane into a solution in dichloromethane to give square colourless tablets, m.p. 374–377 K. Intensity data were recorded for two crystals on a Stoe two-circle diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{\max} 55^\circ$). Crystal

1, mounted about *a* (a diagonal of the square tablet), $0.5 \times 0.5 \times 0.3$ mm, layers 0–8, 2313 reflections; crystal 2, mounted about *c* (the other diagonal), layers 0–9, 2372 reflections. Interlayer scale factors were derived from a least-squares analysis of common reflections. Merging equivalents gave 1565 unique reflections ($R_{\text{int}} = 0.018$, index ranges h 0 to 9, k 0 to 24, l 0 to 10), of which 1288 with $F > 4\sigma(F)$ were used for all calculations *via* program system *SHELXTL* (Sheldrick, 1986). The cell constants were refined from 2θ values of 40 reflections in the range 20 – 24° , measured from crystal 2 on a Stoe–Siemens four-circle diffractometer.

The structure was solved by routine direct methods. Full-matrix least-squares refinement on F proceeded to $R = 0.042$, $wR = 0.048$, for 79 parameters (all non-H atoms anisotropic, C–H included using a riding model, O–H refined with fixed temperature factors but otherwise freely). The weighting scheme was $w^{-1} = \sigma^2(F) + 0.00015F^2$. $S = 2.0$, max. $\Delta/\sigma = 0.04$, max. $\Delta\rho$ within ± 0.018 e \AA^{-3} . Atomic scattering factors were those within *SHELXTL*.

Discussion. Final atomic coordinates are given in Table 1* and derived parameters in Table 2. A thermal ellipsoid plot of (2) ($X = H$) is shown in Fig. 1. Our redetermination confirms the structure analysis of SLH in broad terms, but we note several important differences. (i) We observed no crystal decay. (ii) We obtained many more significant reflections (1288), and thus better e.s.d.'s (typically 0.002–0.003 \AA). (iii) We find a significantly longer *b* axis [19.332 (2), *cf.* (SLH) 19.301 (6) \AA]. Our cell constant e.s.d.'s have been doubled (from those obtained in the refinement) to allow for systematic errors; the e.s.d.'s of SLH may be underestimated. (iv) Our U_{eq} values are systematically lower than those of SLH, by a factor of about 10%. We

* 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 51415 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

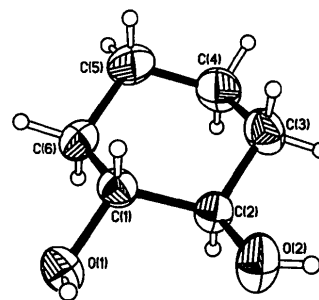


Fig. 1. Molecular structure of (2, $X = H$), showing the atom-numbering scheme.

can offer no explanation for this, unless it is somehow related to the crystal decay they observed. A more detailed comparison of U_{ij} values is not possible because those of SLH are not available.

The positional coordinates agree well for the two structures; the mean difference in fractional coordinates is 0.00029, compared with SLH's mean e.s.d. of 0.00036. The largest difference is 2.5σ for the z coordinate of O(1). Because there are only 24 coordinates a normal probability plot would provide limited information.

A rigid-body libration correction was applied to the title molecule, and indicated individual bond-length corrections of +0.008 for C(1)–O(1), +0.010 for C(3)–C(4) and C(1)–C(6), and +0.009 Å for all other bonds (R_{lib} 0.032). However the derivatives [2], $X \neq H$], which we will compare with the title molecule in the following papers, involve too many degrees of

torsional freedom to allow such a correction. We shall therefore use uncorrected bond lengths in subsequent discussions.

The molecules are linked by hydrogen bonds in layers parallel to the ac plane at $y = 0$ and $\frac{1}{2}$ (see Fig. 2). H-bonding contacts: O(2)···O(1) 2.731 (5), O(2)···H(11) 1.94 (2) Å, O(2)···H(11)–O(1) = 160 (2)° (second atoms at $-x, -y, 1-z$), and O(2)···O(1) 2.778 (5), H(21)···O(1) 2.02 (2) Å, O(2)–H(21)···O(1) = 178 (2)° (second atoms at $\frac{1}{2}-x, -y, \frac{1}{2}+z$).

The diol crystallizes in a regular chair conformation (ring torsion angles all $55.8 \pm 0.6^\circ$). The two C–O bond lengths are equal, at 1.429 (2) Å. However, the OH groups differ in their pattern of H bonding, the O(1)–H bond being approximately antiperiplanar to C(1)–C(6), whereas O(2)–H is close to antiperiplanar to C(1)–C(2). As a result there are small differences in bond and torsion angles at C(1) and C(2) (Fig. 3), and thus two slightly different standard geometries on which to base comparisons with unsymmetrical derivatives (2).

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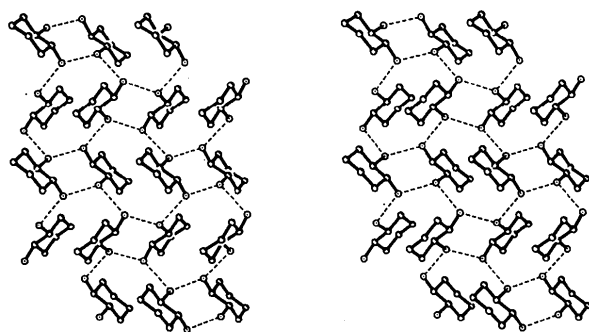


Fig. 2. Packing diagram, showing pattern of hydrogen bonding parallel to the ac plane at $y = \frac{1}{2}$.

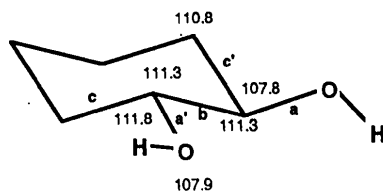


Fig. 3. Differences in the geometries about C(1) and C(2). The torsion angles abc and $a'bc'$ are $175.5(2)$ and $178.7(2)^\circ$, respectively.

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

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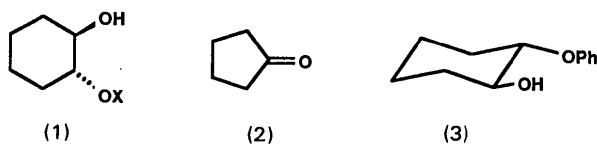
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Abstract. $C_{12}H_{16}O_2$, $M_r = 192.26$, monoclinic, $P2_1/c$, $a = 5.420$ (2), $b = 20.634$ (5), $c = 19.136$ (4) Å, $\beta = 93.45$ (2)°, $V = 2136$ Å³, $Z = 8$, $D_x = 1.195$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.075$ mm⁻¹, $F(000) = 832$, $T = 293$ 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 (Å² × 10³)

	x	y	z	U_{eq} *
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 $K\alpha$ radiation ($2\theta_{max} = 50^\circ$). 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 $F > 4\sigma(F)$ 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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