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—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.

We thank the Fonds der Chemischen Industrie and the Cambridge Philosophical Society for support.

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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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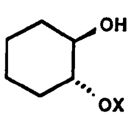
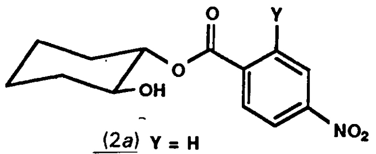
Abstract. The 4-nitrobenzoate ester (2*a*): $C_{13}H_{15}NO_5$, $M_r = 265{\cdot}26$, triclinic, $P\bar{1}$, $a = 5{\cdot}659\,(2)$, $b = 8{\cdot}167\,(2)$, $c = 14{\cdot}167\,(4)$ Å, $\alpha = 91{\cdot}94\,(3)$, $\beta = 101{\cdot}37\,(2)$, $\gamma = 90{\cdot}81\,(2)°$, $V = 641{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}37$ Mg m^{-3}, $F(000) = 280$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}1$ mm^{-1}, $T = 293$ K. The structure was refined to $R = 0{\cdot}045$ for 2215 unique observed reflections. The ester C—O*X* 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 (2*b*): $C_{13}H_{14}N_2O_7$, $M_r = 310{\cdot}26$, triclinic, $P\bar{1}$, $a = 7{\cdot}562\,(2)$, $b = 8{\cdot}352\,(2)$, $c = 12{\cdot}790\,(2)$ Å, $\alpha = 91{\cdot}73\,(2)$, $\beta = 100{\cdot}83\,(2)$, $\gamma = 116{\cdot}33\,(1)°$, $V = 705{\cdot}2$ Å^3, $Z = 2$, $D_x = 1{\cdot}46$ Mg m^{-3}, $F(000) = 324$, $\mu = 0{\cdot}11$ mm^{-1}, $T = 293$ K. The structure was refined to $R = 0{\cdot}046$ for 2327 unique observed reflections. The ester C—O*X* 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* = H] and its monophenyl ether [(1), *X* = Ph] (Jones, Edwards & Kirby, 1989*a*,*b*). This paper deals with two monoesters, the 4-nitrobenzoate (2*a*) and the 2,4-dinitrobenzoate (2*b*).



(1)



(2*a*) Y = H
(2*b*) Y = NO_2

Experimental. The 4-nitrobenzoate (2*a*) 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 (2*b*) was obtained from the diol and 2,4-dinitrobenzoic acid in Et_2O/tetrahydrofuran, using dicyclohexyl carbodiimide as

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

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condensing agent. Diffusion of petrol into a solution in diisopropyl ether gave pale yellow blocks, m.p. 357–359 K, dec.

(2*a*) Crystal 0·55 × 0·45 × 0·35 mm, sealed in a glass capillary. 3148 profile-fitted intensities were registered on a Stoe–Siemens four-circle diffractometer using monochromated Mo $K\alpha$ radiation to a $2\theta_{\max}$ of 55° (Clegg, 1981). Three check reflections showed no significant intensity change. Merging equivalents gave 2944 unique reflections ($R_{\rm int} = 0{\cdot}013$: index ranges after merging h −7 to 7, k −10 to 10, l 0 to 18), of which 2215 with $F > 4\sigma(F)$ were used for all calculations *via* program system *SHELXTL* (Sheldrick, 1986). Cell constants were refined from 2θ values of 30 reflections in the range 20–23°.

The structure was solved by routine direct methods and subjected to cascade least-squares refinement on F. All non-H atoms were refined anisotropically, C—H using a riding model. The final R value was 0·045, with $wR = 0{\cdot}054$; the weighting scheme was $w^{-1} = \sigma^2(F) + 0{\cdot}0002F^2$. 175 parameters, $S = 2{\cdot}1$, max. Δ/σ 0·08, max. $\Delta\rho$ within $\pm 0{\cdot}16$ e Å^{-3}.

(2*b*) Data collection, structure solution and refinement as for (2*a*), with the following differences. Crystal 0·55 × 0·4 × 0·35 mm, 4620 reflections measured, 3222 unique ($R_{\rm int} = 0{\cdot}015$, index ranges h −9 to 9, k −10 to 10, l 0 to 16), 2327 observed. Cell constants refined from 60 2θ values. Refinement to $R = 0{\cdot}046$, $wR = 0{\cdot}049$; 202 parameters, $S = 1{\cdot}8$, max. Δ/σ 0·001, max. $\Delta\rho$ within $\pm 0{\cdot}18$ e Å^{-3}.

Discussion. Final atom coordinates appear in Table 1* and derived parameters in Table 2. Thermal ellipsoid plots of (2*a*) and (2*b*) are shown in Fig. 1(*a*), (*b*).

Esters (2*a*) and (2*b*) crystallize in similar conformations, although the ester groups can be seen to be rotated slightly (Fig. 1*c*) when the two structures are superimposed. The ester groups are *Z*, as is normal. The cyclohexane chair of (2*a*) shows the slight increase in puckering noted for the phenyl ether [(1), X = Ph: Jones, Edwards & Kirby (1989*b*)], but this has disappeared in (2*b*), which has all ring torsion angles 55·0 ± 0·8° and is not significantly different in this respect from the parent diol (Jones, Edwards & Kirby, 1989*a*). Evidently this is not a feature of relevance to incipient rearrangement.

Both compounds display hydrogen bonding. In (2*a*) (Fig. 2*a*) the molecules are linked parallel to the short axis by O(3)···O(2) 2·916 (3), O(3)···H(2) 2·15 (2) Å, O—H···O 168 (2)° (second atoms at $-1 + x, y, z$). An additional short contact is O(2)—N 3·18 Å (N at $1-x$,

Table 1. *Atom coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2×10^3)

	x	y	z	$U_{\rm eq}$*
(*a*) Compound (2*a*)				
C(11)	2563 (2)	2158 (2)	7492 (1)	41 (1)
C(12)	5140 (2)	1703 (2)	7898 (1)	43 (1)
C(13)	5348 (3)	1292 (2)	8947 (1)	52 (1)
C(14)	4589 (3)	2716 (2)	9527 (1)	62 (1)
C(15)	2026 (3)	3210 (2)	9106 (1)	61 (1)
C(16)	1774 (3)	3597 (2)	8044 (1)	51 (1)
C(21)	669 (2)	2530 (2)	4847 (1)	41 (1)
C(22)	2741 (3)	3223 (2)	4627 (1)	50 (1)
C(23)	2932 (3)	3382 (2)	3673 (1)	51 (1)
C(24)	1044 (3)	2811 (2)	2962 (1)	42 (1)
C(25)	−1040 (3)	2142 (2)	3157 (1)	47 (1)
C(26)	−1220 (2)	2005 (2)	4112 (1)	47 (1)
N	1312 (2)	2894 (2)	1947 (1)	55 (1)
O(41)	3066 (2)	3622 (2)	1781 (1)	76 (1)
O(42)	−244 (2)	2238 (2)	1332 (1)	82 (1)
C(1)	418 (2)	2271 (2)	5862 (1)	44 (1)
O(1)	2481 (2)	2555 (1)	6485 (1)	49 (1)
O(2)	5850 (2)	329 (1)	7383 (1)	56 (1)
O(3)	−1448 (2)	1833 (2)	6074 (1)	63 (1)
(*b*) Compound (2*b*)				
C(11)	3483 (2)	−770 (2)	2035 (1)	41 (1)
C(12)	4722 (2)	−1605 (2)	1688 (1)	40 (1)
C(13)	3380 (3)	−3245 (2)	865 (1)	50 (1)
C(14)	2209 (3)	−2797 (2)	−78 (1)	55 (1)
C(15)	988 (3)	−1947 (2)	277 (1)	61 (1)
C(16)	2324 (3)	−291 (2)	1108 (1)	56 (1)
O(1)	4930 (2)	875 (1)	2768 (1)	42 (1)
O(2)	5676 (2)	−2136 (1)	2584 (1)	51 (1)
C(10)	4235 (2)	1464 (2)	3487 (1)	45 (1)
O(10)	2571 (2)	693 (2)	3659 (1)	76 (1)
C(21)	5824 (2)	3210 (2)	4148 (1)	41 (1)
C(22)	7058 (2)	4748 (2)	3748 (1)	40 (1)
C(23)	8499 (2)	6291 (2)	4403 (1)	42 (1)
C(24)	8679 (2)	6275 (2)	5493 (1)	43 (1)
C(25)	7484 (3)	4801 (2)	5933 (1)	49 (1)
C(26)	6063 (3)	3281 (2)	5251 (1)	48 (1)
N(2)	6806 (3)	4817 (2)	2582 (1)	55 (1)
O(21)	5097 (2)	4011 (2)	2027 (1)	72 (1)
O(22)	8315 (3)	5699 (2)	2250 (1)	87 (1)
N(4)	10224 (2)	7902 (2)	6217 (1)	52 (1)
O(41)	10407 (2)	7868 (2)	7182 (1)	77 (1)
O(42)	11236 (2)	9202 (2)	5804 (1)	64 (1)

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

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *for* (2*a*) *and* (2*b*)

	(2*a*)	(2*b*)
C(11)—C(12)	1·514 (3)	1·509 (4)
C(11)—C(16)	1·510 (3)	1·511 (4)
C(11)—O(1)	1·466 (3)	1·473 (3)
C(12)—C(13)	1·517 (3)	1·514 (3)
C(12)—O(2)	1·424 (3)	1·426 (3)
C(13)—C(14)	1·517 (3)	1·516 (4)
C(14)—C(15)	1·521 (3)	1·511 (3)
C(15)—C(16)	1·526 (3)	1·527 (3)
C(1)—O(1)*	1·330 (3)	1·321 (3)
C(1)—O(3)*	1·206 (3)	1·200 (3)
C(1)—C(21)*	1·495 (3)	1·509 (3)
C(21)—C(22)	1·389 (3)	1·392 (3)
C(21)—C(26)	1·389 (3)	1·384 (3)
C(22)—C(23)	1·387 (3)	1·377 (3)
C(22)—N(2)		1·474 (3)
C(23)—C(24)	1·380 (3)	1·376 (3)
C(24)—C(25)	1·373 (3)	1·377 (3)
C(24)—N*	1·478 (3)	1·476 (3)
C(25)—C(26)	1·385 (3)	1·378 (3)

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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 51417 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 (*cont.*)

	(2*a*)	(2*b*)
N(2)–O(21)		1·218 (3)
N(2)–O(22)		1·217 (3)
N–O(41)*	1·216 (3)	1·219 (3)
N–O(42)*	1·214 (3)	1·222 (3)
O(2)–H(2)	0·775 (8)	0·80 (2)
C(12)–C(11)–C(16)	111·9 (2)	113·1 (3)
C(12)–C(11)–O(1)	106·3 (2)	106·1 (2)
C(16)–C(11)–O(1)	110·7 (2)	109·6 (2)
C(11)–C(12)–C(13)	108·9 (2)	110·1 (2)
C(11)–C(12)–O(2)	111·4 (2)	110·7 (2)
C(13)–C(12)–O(2)	109·2 (2)	108·8 (2)
C(12)–C(13)–C(14)	111·2 (2)	111·6 (3)
C(13)–C(14)–C(15)	110·9 (2)	111·9 (3)
C(14)–C(15)–C(16)	110·7 (2)	111·2 (2)
C(11)–C(16)–C(15)	110·2 (2)	110·2 (2)
C(11)–O(1)–C(1)*	117·2 (2)	117·4 (2)
O(1)–C(1)–O(3)*	124·9 (2)	125·7 (2)
C(21)–C(1)–O(1)*	112·1 (2)	112·5 (2)
C(21)–C(1)–O(3)*	123·0 (2)	121·7 (3)
C(22)–C(21)–C(1)*	122·0 (2)	125·9 (2)
C(26)–C(21)–C(1)*	117·9 (2)	116·7 (2)
C(22)–C(21)–C(26)	120·1 (2)	117·5 (2)
C(21)–C(22)–C(23)	120·0 (2)	122·7 (2)
C(21)–C(22)–N(2)		120·7 (2)
C(23)–C(22)–N(2)		116·6 (2)
C(22)–C(23)–C(24)	118·4 (2)	117·2 (2)
C(23)–C(24)–C(25)	122·9 (2)	122·7 (2)
C(23)–C(24)–N*	118·2 (2)	118·5 (2)
C(25)–C(24)–N*	118·9 (2)	118·8 (2)
C(24)–C(25)–C(26)	118·2 (2)	118·4 (3)
C(21)–C(26)–C(25)	120·5 (2)	121·6 (3)
C(22)–N(2)–O(21)		117·4 (3)
C(22)–N(2)–O(22)		117·6 (2)
O(21)–N(2)–O(22)		125·0 (3)
C(24)–N–O(41)*	118·0 (2)	118·3 (2)
C(24)–N–O(42)*	117·8 (2)	117·4 (2)
O(41)–N–O(42)*	124·4 (2)	124·3 (2)
C(12)–O(2)–H(2)	106·1 (1)	
C(16)–C(11)–C(12)–C(13)	58·5 (3)	−55·8 (3)
C(16)–C(11)–C(12)–O(2)	179·0 (2)	−176·2 (2)
O(1)–C(11)–C(12)–C(13)	179·5 (2)	−176·0 (2)
O(1)–C(11)–C(12)–O(2)	−60·1 (2)	63·6 (2)
C(12)–C(11)–C(16)–C(15)	−57·8 (3)	55·6 (3)
O(1)–C(11)–C(16)–C(15)	−176·2 (2)	173·7 (3)
C(12)–C(11)–O(1)–C(1)	150·0 (2)	−154·5 (2)
C(16)–C(11)–O(1)–C(1)	−88·3 (2)	83·1 (3)
C(11)–C(12)–C(13)–C(14)	−57·7 (3)	54·7 (3)
O(2)–C(12)–C(13)–C(14)	−179·5 (2)	176·2 (3)
C(12)–C(13)–C(14)–C(15)	57·2 (3)	−55·3 (3)
C(13)–C(14)–C(15)–C(16)	−55·4 (3)	54·8 (3)
C(14)–C(15)–C(16)–C(11)	55·4 (3)	−54·2 (3)
O(3)–C(1)–O(1)–C(11)*	6·3 (3)	7·0 (4)
C(21)–C(1)–O(1)–C(11)*	−172·9 (2)	−176·8 (2)
C(22)–C(21)–C(1)–O(1)*	−8·9 (3)	−50·0 (4)
C(26)–C(21)–C(1)–O(1)*	169·0 (2)	−130·3 (3)
C(22)–C(21)–C(1)–O(3)*	172·0 (3)	−133·6 (3)
C(26)–C(21)–C(1)–O(3)*	−10·1 (3)	46·2 (4)
C(1)–C(21)–C(22)–C(23)	177·5 (2)	−179·1 (3)
C(1)–C(21)–C(26)–C(25)	−176·9 (2)	179·3 (3)
C(10)–C(21)–C(22)–N(2)		3·7 (4)
C(26)–C(21)–C(22)–N(2)		−176·1 (3)
N(2)–C(22)–C(23)–C(24)		176·8 (3)
C(21)–C(22)–N(2)–O(21)		34·0 (4)
C(21)–C(22)–N(2)–O(22)		−147·2 (3)
C(23)–C(22)–N(2)–O(21)		−143·4 (3)
C(23)–C(22)–N(2)–O(22)		35·5 (4)
C(22)–C(23)–C(24)–N*	−176·5 (2)	179·4 (3)
N–C(24)–C(25)–C(26)*	177·1 (2)	−179·2 (3)
C(23)–C(24)–N–O(41)*	−7·9 (3)	−178·5 (3)
C(23)–C(24)–N–O(42)*	172·5 (2)	1·6 (4)
C(25)–C(24)–N–O(41)*	173·4 (2)	1·3 (4)
C(25)–C(24)–N–O(42)*	−6·1 (3)	−178·6 (3)

Sign convention as defined by Klyne & Prelog (1960). *C(1), N and O(3) become C(10), N(4) and O(10), respectively, in (2*b*).

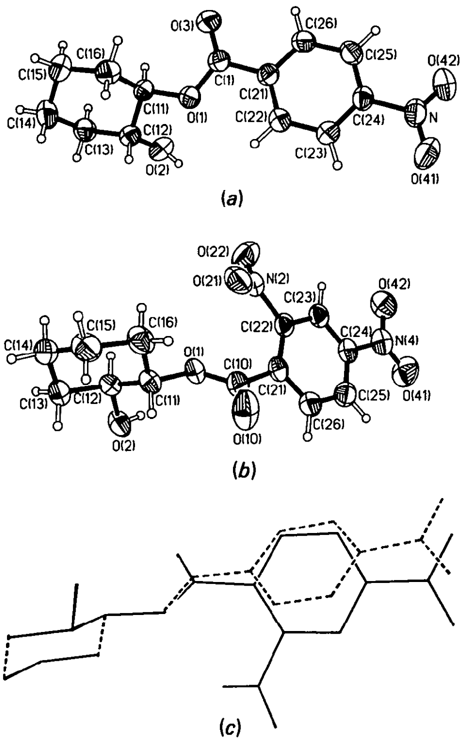

Fig. 1. (*a*) Molecular structure of (2*a*), showing the atom-numbering scheme. (*b*) Molecular structure of (2*b*), showing the atom-numbering scheme. (*c*) Superposition of (2*a*) and (2*b*), showing the close similarities of conformation.

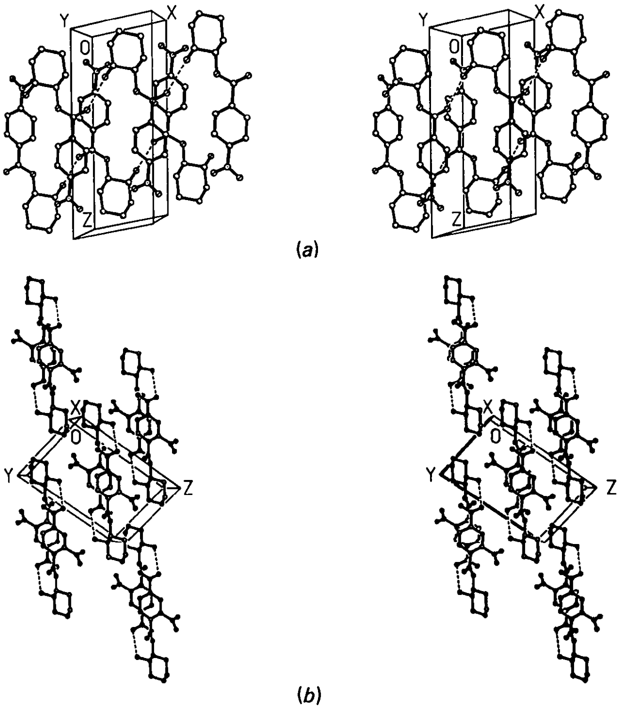

Fig. 2. (*a*) Packing diagram for (2*a*), showing the pattern of hydrogen bonding. (*b*) Packing diagram for (2*b*), showing the pattern of hydrogen bonding.

$-y$, $1-z$). In (2*b*) (Fig. 2*b*), on the other hand, the molecules are linked in pairs by the H bond O(42)···O(2) 2·919 (3), O(42)···H(O2) 2·14 (2) Å, O—H···O 165 (2)° (second atoms at $2-x$, $1-y$, $1-z$), and there are also several other short contacts, *e.g.* N(4)···O(10) 2·858 (3) Å [O(10) at $1-x$, $1-y$, $1-z$].

The ester C—O*X* bonds show the expected lengthening compared with the parent diol (Allen & Kirby, 1984): C(11)—O(1) is 1·466 (3) Å in (2*a*) and 1·473 (3) Å in (2*b*), reflecting the lower pK_a of 2,4-dinitrobenzoic acid, which is 1·425 (Dippy, Hawkins & Smith, 1964) compared with 3·44 for 4-nitrobenzoic acid. [The C—OH bond length in the parent diol is 1·429 (2) Å (Jones, Edwards & Kirby, 1989*a*).] This correlation is discussed for the full set of eight structures in the following paper (Jones, Edwards & Kirby, 1989*c*), where the data are also analysed in the light of the geometrical changes expected for the pinacol rearrangement. In this context it should be noted that the best match of torsion angles, with the parent diol, about the CH—O bonds of (2*a*) and (2*b*), is obtained by comparing C(11)—O(1) with C(2)—O(2) of the diol. The O—H bonds are roughly antiperiplanar to C(13)—C(14), corresponding to the O(1)—H bond of the diol.

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Bond Length and Reactivity. The Pinacol Rearrangement. 4.* Structures of *trans*-2-Hydroxycyclohexyl Benzenesulfonate, *p*-Toluenesulfonate and 2-Naphthalenesulfonate

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Abstract. The benzenesulfonate ester (4*a*), $C_{12}H_{16}O_4S$, $M_r = 256·32$, monoclinic, $P2_1/c$, $a = 5·6404\,(8)$, $b = 19·006\,(3)$, $c = 11·455\,(2)$ Å, $\beta = 94·58\,(2)$°, $V = 1224·0$ Å^3, $Z = 4$, $D_x = 1·39$ Mg m^{-3}, $F(000) = 544$, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 0·25$ mm^{-1}, $T = 293$ K, $R = 0·047$ for 2317 unique observed reflections. The toluenesulfonate ester (4*b*), $C_{13}H_{18}O_4S$, $M_r = 270·34$, monoclinic, $P2_1/c$, $a = 5·680\,(1)$, $b = 18·656\,(4)$, $c = 12·761\,(3)$ Å, $\beta = 94·25\,(2)$° [(4*a*) and (4*b*) are essentially isostructural], $V = 1348·5$ Å^3, $Z = 4$, $D_x = 1·33$ Mg m^{-3}, $F(000) = 576$, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 0·23$ mm^{-1}, $T = 293$ K, $R = 0·055$ for 2148 reflections. The naphthalenesulfonate ester (5), $C_{16}H_{18}O_4S$, $M_r = 306·38$, monoclinic, $P2_1$, $a = 9·399\,(3)$, $b = 6·218\,(2)$, $c = 13·614\,(3)$ Å, $\beta = 109·17\,(2)$°, $V = 751·6$ Å^3, $Z = 2$, $D_x = 1·35$ Mg m^{-3}, $F(000) = 324$, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 0·22$ mm^{-1}, $T = 293$ K, $R = 0·049$ for 1963 reflections. The absolute structure of (5) was determined with an η-refinement. The changes in geometry observed over the series of derivatives of *trans*-cyclohexane-1,2-diol described in this and the three preceding papers [Jones, Edwards & Kirby (1989). *Acta Cryst.* C**45**, 244–246, 247–249, 249–252] can be explained in terms of an incipient S_N1 reaction. Changes at the adjacent C—OH centre are not significant.

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* Part 3: Jones, Edwards & Kirby (1989*c*).

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