−y, 1−z). In (2b) (Fig. 2b), 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−OX bonds show the expected lengthening compared with the parent diol (Allen & Kirby, 1984): C(11)−O(1) is 1·466 (3) Å in (2a) and 1·473 (3) Å in (2b), 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, 1989a).] This correlation is discussed for the full set of eight structures in the following paper (Jones, Edwards & Kirby, 1989c), 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 (2a) and (2b), 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.

References

ALLEN, F. H. & KIRBY, A. J. (1984). J. Am. Chem. Soc. 106, 6197–6200.
CLEGG, W. (1981). Acta Cryst. A37, 22–28.
DIPPY, J. E. J., HAWKINS, B. V. & SMITH, B. D. (1964). J. Chem. Soc. pp. 154–163.
JONES, P. G., EDWARDS, M. R. & KIRBY, A. J. (1989a). Acta Cryst. C45, 244–246.
JONES, P. G., EDWARDS, M. R. & KIRBY, A. J. (1989b). Acta Cryst. C45, 247–249.
JONES, P. G., EDWARDS, M. R. & KIRBY, A. J. (1989c). Acta Cryst. C45, 252–257.
KLYNE, W. & PRELOG, V. (1960). Experientia, 16, 521–523.
LOIBNER, H. & ZBIRAL, E. (1976). Helv. Chim. Acta, 59, 2100–2113.
SHELDRICK, G. M. (1986). SHELXTL. Program for solving, refining and displaying crystal structures. Nicolet Corp., Madison, Wisconsin, USA.

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 (4a), $C_{12}H_{16}O_4S$, $M_r = 256.32$, monoclinic, $P2_1/c$, $a = 5.6404$ (8), $b = 19.006$ (3), $c = 11.455$ (2) Å, $\beta = 94.58$ (2)°, $V = 1224.0$ Å³, $Z = 4$, $D_x = 1.39$ 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 (4b), $C_{13}H_{18}O_4S$, $M_r = 270.34$, monoclinic, $P2_1/c$, $a = 5.680$ (1), $b = 18.656$ (4), $c = 12.761$ (3) Å, $\beta = 94.25$ (2)° [(4a) and (4b) are essentially isostructural], $V = 1348.5$ Å³, $Z = 4$, $D_x = 1.33$ 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)°, $V = 751.6$ Å³, $Z = 2$, $D_x = 1.35$ 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. C45, 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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Introduction. Our work on bond length–reactivity correlations (Jones & Kirby, 1979, 1984, 1986) raises the intriguing possibility that we may be able to observe changes in ground-state geometry, corresponding to the initial changes of familiar heterolytic reactions, by comparing crystal structures of suitable series of compounds. So far we have found convincing evidence of such changes for acetal cleavage (Jones & Kirby, 1979), for an incipient fragmentation reaction (Jones & Kirby, 1982), and for the S_N1 reaction of a benzylic system (Edwards, Jones & Kirby, 1986). We have also observed changes in the expected direction for the Beckmann rearrangement of a series of derivatives of oxime (1) (Edwards, Kirby, Raithby & Jones, 1987).
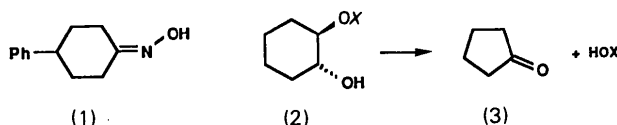
We are currently looking at a series of derivatives (2) of *trans*-cyclohexane-1,2-diol, which are known to undergo the pinacol rearrangement [(2)→(3)] when XO^- is a good enough leaving group. We have reported structures for the parent diol (Jones, Edwards & Kirby, 1989a), the monophenyl ether [(2), $X = $ Ph (Jones, Edwards & Kirby, 1989b)] and two esters, the 4-nitrobenzoate and the 2,4-dinitrobenzoate (Jones, Edwards & Kirby, 1989c). The most interesting compounds in a series of this sort are often those with the best leaving groups, because they are the most reactive (sometimes, indeed, too reactive to be crystallized). Also, we find an average of about two crystalline compounds in three to be unsuitable for accurate structure determination. Accordingly, in the present series we prepared three monoarenesulfonate esters, (4a), (4b) and (5). Most unusually, all three gave good structures, which are reported here.

(4a), R=H
(4b) R=Me

(5)
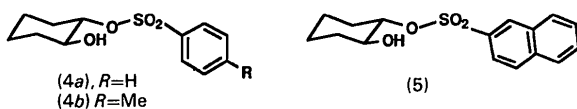
Experimental. The benzenesulfonate (4a) was prepared by adding benzenesulfonic acid to cyclohexene oxide in diethyl ether. Diffusion of petrol into a solution in dichloromethane gave colourless rectangular prisms, m.p. 361–362 K. (4b) and (5) were obtained from the diol [(2), $X = $ H] and the sulfonyl chloride in pyridine. (4b) gave colourless prisms, m.p. 368–369 K [lit. 362–363 K (Trimmell, Stout, Doane, Russell, Beringer, Saul & Van Gessel, 1975)] on diffusing hexane into a solution in diisopropyl ether. (5) was crystallized by diffusing pentane into a solution in diethyl ether, and gave colourless prisms, m.p. 367–369 K dec.

(4a). A crystal $0.65 \times 0.4 \times 0.2$ mm, cut from a much longer prism, was mounted in a glass capillary. 3960 profile-fitted intensities (Clegg, 1981) were recorded on a Stoe–Siemens four-circle diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{max} = 55°$). Three check reflections showed no significant intensity change. Merging equivalents gave 2812 unique reflections ($R_{int} = 0.014$, index ranges after merging h −7 to 7, k 0 to 24, l 0 to 14), of which 2317 with $F > 4\sigma(F)$ were used for all calculations *via* program system SHELXTL (Sheldrick, 1986). Scattering factors used were those stored in the SHELXTL program. Cell constants were refined from 2θ values of 38 reflections in the range 20–23°.

The structure was solved by routine direct methods and subjected to anisotropic cascade least-squares refinement on F. H atoms were included using a riding model, except for the hydroxyl H, which was refined subject to the constraint O—H = 0.8 Å, with a weight corresponding to an e.s.d. of 0.02 Å. Although the hydroxyl H was identified from difference syntheses, there is some uncertainty as to its reliability because of difficulties in interpreting the hydrogen-bonding pattern (see below). The final R value was 0.047 with $wR = 0.054$; the weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$, with $g = 0.00025$. 157 parameters; $S = 2.1$, max. Δ/σ 0.02, max. $\Delta\rho$ within ± 0.22 e Å^{-3}.

(4b). As for (4a), with the following differences: crystal $0.6 \times 0.25 \times 0.1$ mm; 4238 intensities, 3106 unique ($R_{int} = 0.016$, index range l 0 to 16), 2148 observed. Cell constant refinement using 34 reflections. Structure refinement to $R = 0.055$, with $wR = 0.054$; $g = 0.0003$; 169 parameters; $S = 1.6$, max. Δ/σ 0.033. Similar problems were experienced with the refinement of the hydroxyl H.

(5). As for (4a) with the following differences: crystal $0.45 \times 0.3 \times 0.15$ mm; 2817 intensities to $2\theta_{max} = 50°$, 2649 unique (Friedel opposites not merged; $R_{int} = 0.028$, index range h −10 to 10, k −7 to 7, l 0 to 16), 1963 observed. Cell constants refined from 40 2θ values. Structure refinement to $R = 0.049$, $wR = 0.044$. Absolute structure determined by an η refinement (Rogers, 1981); $\eta = -1.0$ (2), after which the structure was inverted. 192 parameters; $S = 1.3$, $g = 0.0003$, max. Δ/σ 0.01, max. $\Delta\rho$ within ± 0.28 e Å^{-3}. No problems were experienced with the refinement of the hydroxyl H.

Discussion. Final atom coordinates appear in Table 1,* with derived parameters in Table 2. Thermal-ellipsoid plots of (4a), (4b) and (5) and a superposition of (4a)

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* 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 51418 (59 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	x	y	z	U_{eq}*
(a) Compound (4a)				
S	4179 (1)	6225 (1)	2184 (1)	35 (1)
O(1)	4763 (2)	6303 (1)	3540 (1)	35 (1)
O(2)	7567 (3)	5319 (1)	4918 (1)	51 (1)
O(3)	5575 (3)	6706 (1)	1575 (1)	48 (1)
O(4)	1650 (2)	6264 (1)	2033 (1)	51 (1)
C(11)	7213 (3)	6472 (1)	4004 (1)	31 (1)
C(12)	7677 (3)	6059 (1)	5125 (2)	35 (1)
C(13)	10109 (4)	6253 (1)	5697 (2)	45 (1)
C(14)	10344 (4)	7038 (1)	5923 (2)	54 (1)
C(15)	9828 (4)	7451 (1)	4800 (2)	53 (1)
C(16)	7393 (4)	7256 (1)	4212 (2)	43 (1)
C(21)	5042 (3)	5359 (1)	1875 (1)	33 (1)
C(22)	3617 (4)	4812 (1)	2180 (2)	44 (1)
C(23)	4198 (4)	4132 (1)	1889 (2)	52 (1)
C(24)	6178 (4)	4003 (1)	1303 (2)	53 (1)
C(25)	7618 (4)	4553 (1)	1014 (2)	54 (1)
C(26)	7067 (3)	5239 (1)	1292 (2)	43 (1)
(b) Compound (4b)				
S	4338 (1)	6601 (1)	3015 (1)	45 (1)
O(1)	4988 (3)	6465 (1)	4213 (1)	42 (1)
O(2)	7574 (3)	5295 (1)	5126 (2)	57 (1)
O(3)	5667 (3)	7191 (1)	2660 (1)	57 (1)
O(4)	1820 (3)	6631 (1)	2939 (1)	61 (1)
C(11)	7451 (4)	6556 (1)	4650 (2)	36 (1)
C(12)	7793 (4)	6008 (1)	5523 (2)	40 (1)
C(13)	10204 (4)	6100 (1)	6095 (2)	50 (1)
C(14)	10602 (5)	6857 (1)	6510 (2)	56 (1)
C(15)	10261 (5)	7389 (1)	5623 (2)	54 (1)
C(16)	7825 (5)	7315 (1)	5051 (2)	48 (1)
C(21)	5216 (4)	5821 (1)	2381 (2)	43 (1)
C(22)	3883 (5)	5205 (1)	2424 (2)	59 (1)
C(23)	4497 (5)	4601 (1)	1897 (2)	67 (1)
C(24)	6458 (5)	4595 (2)	1314 (2)	61 (1)
C(25)	7776 (5)	5208 (2)	1295 (2)	67 (1)
C(26)	7191 (5)	5824 (2)	1816 (2)	58 (1)
C(27)	7141 (7)	3927 (2)	729 (3)	89 (1)
(c) Compound (5)				
S	7936 (1)	3000	3243 (1)	53 (1)
O(1)	8384 (2)	4347 (4)	4269 (2)	50 (1)
O(3)	7361 (3)	953 (4)	3405 (2)	71 (1)
O(4)	9222 (3)	3153 (6)	2908 (2)	78 (1)
C(11)	7592 (4)	4109 (5)	5034 (3)	44 (1)
C(12)	7377 (4)	6231 (5)	5414 (3)	48 (1)
O(2)	6369 (3)	7474 (5)	4599 (2)	78 (1)
C(13)	6705 (5)	6039 (6)	6288 (3)	64 (2)
C(14)	7643 (5)	4614 (7)	7160 (3)	71 (2)
C(15)	7842 (5)	2404 (6)	6754 (3)	69 (2)
C(16)	8540 (4)	2604 (6)	5881 (3)	58 (2)
C(21)	5089 (4)	3623 (5)	1959 (2)	44 (1)
C(22)	6475 (3)	4496 (5)	2368 (2)	43 (1)
C(23)	6820 (4)	6561 (6)	2082 (3)	52 (2)
C(24)	5724 (4)	7660 (5)	1349 (3)	52 (2)
C(24a)	4275 (4)	6824 (5)	880 (3)	44 (1)
C(25)	3140 (5)	7909 (7)	84 (3)	61 (2)
C(26)	1754 (5)	7011 (7)	−378 (3)	70 (2)
C(27)	1435 (4)	5007 (8)	−56 (3)	73 (2)
C(28)	2489 (4)	3894 (6)	711 (3)	61 (2)
C(28a)	3934 (4)	4761 (6)	1186 (2)	45 (1)

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

and (4b) are shown in Fig. 1. Fig. 2 shows the packing diagrams for (5) and (4a).

The molecular packing of (5) involves H bonding between the hydroxyl group and a sulfonate oxygen of a translationally related molecule (Fig. 2a); associated

distances are $H(O2)\cdots O(3)$ 2·17 (5), $O(2)\cdots O(3)$ 3·031 (6) Å, $O-H\cdots O$ 147 (3)°, with second atoms at $(x, 1+y, z)$. In (4a) and (4b) there is less clear-cut evidence for hydrogen bonding (Fig. 2b); the shortest $O\cdots O$ contact in (4a) is 2·99 Å between O(2) and its symmetry equivalent at $2-x, -y, -z$, but this does not involve any $H\cdots O$ contact. A slightly longer contact to a further equivalent at $1-x, 1-y, 1-z$ (3·16 Å) involves $H\cdots O$ 2·44 Å, but also $H\cdots H$ 1·75 Å, which

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *for compounds* (4a), (4b) *and* (5)

	(4a)	(4b)	(5)
O(1)—S	1·569 (2)	1·566 (3)	1·563 (3)
O(3)—S	1·424 (3)	1·427 (3)	1·428 (4)
O(4)—S	1·425 (3)	1·427 (3)	1·428 (4)
C(11)—O(1)	1·476 (3)	1·476 (3)	1·480 (6)
C(11)—C(12)	1·509 (3)	1·514 (4)	1·506 (6)
C(11)—C(16)	1·511 (3)	1·516 (4)	1·490 (5)
C(12)—O(2)	1·428 (3)	1·425 (4)	1·427 (5)
C(12)—C(13)	1·518 (4)	1·513 (4)	1·523 (7)
C(13)—C(14)	1·518 (4)	1·520 (4)	1·512 (6)
C(14)—C(15)	1·515 (4)	1·507 (5)	1·516 (7)
C(15)—C(16)	1·526 (4)	1·522 (5)	1·540 (8)
C(21)—S*	1·761 (3)	1·756 (3)	1·760 (4)
C(21)—C(22)*	1·376 (4)	1·379 (5)	1·410 (6)
C(21)—C(26)*	1·386 (4)	1·378 (5)	1·351 (5)
C(22)—C(23)*	1·380 (4)	1·371 (5)	1·360 (6)
C(23)—C(24)*	1·370 (4)	1·384 (5)	1·401 (6)
C(24)—C(25)*	1·380 (4)	1·368 (5)	1·418 (6)
C(24)—C(27)		1·517 (5)	
C(25)—C(26)*	1·384 (4)	1·381 (5)	1·427 (5)
C(24a)—C(25)			1·417 (6)
C(25)—C(26)			1·366 (7)
C(26)—C(27)			1·386 (8)
C(27)—C(28)			1·367 (6)
C(28)—C(28a)			1·406 (6)
O(1)—S—O(3)	110·1 (2)	110·0 (2)	110·1 (2)
O(1)—S—O(4)	104·1 (2)	103·7 (2)	104·0 (2)
O(3)—S—O(4)	119·6 (2)	119·9 (2)	120·8 (3)
O(1)—S—C(21)*	104·4 (2)	105·2 (2)	104·0 (2)
O(3)—S—C(21)*	109·2 (2)	108·5 (2)	108·9 (3)
O(4)—S—C(21)*	108·3 (2)	108·6 (2)	107·7 (3)
S—O(1)—C(11)	119·6 (2)	119·9 (2)	120·4 (3)
O(1)—C(11)—C(12)	106·7 (2)	105·5 (3)	105·7 (4)
O(1)—C(11)—C(16)	108·7 (2)	109·8 (3)	108·3 (4)
C(12)—C(11)—C(16)	111·9 (2)	112·0 (3)	112·8 (4)
O(2)—C(12)—C(11)	111·7 (2)	111·4 (3)	110·9 (4)
O(2)—C(12)—C(13)	109·7 (2)	109·2 (3)	108·1 (4)
C(11)—C(12)—C(13)	109·3 (3)	109·9 (3)	109·5 (4)
C(12)—C(13)—C(14)	112·1 (3)	112·3 (3)	112·0 (5)
C(13)—C(14)—C(15)	110·8 (3)	110·1 (3)	110·8 (4)
C(14)—C(15)—C(16)	110·7 (3)	111·2 (3)	110·1 (5)
C(11)—C(-6)—C(-5)	110·9 (3)	110·3 (3)	110·3 (4)
S—C(21)—C(22)*	118·6 (2)	119·8 (3)	118·0 (3)
S—C(21)—C(26)*	120·2 (2)	120·5 (3)	120·0 (4)
C(22)—C(21)—C(26)*	121·2 (3)	119·7 (3)	122·0 (3)
C(21)—C(22)—C(23)*	119·4 (3)	120·3 (4)	118·2 (4)
C(22)—C(23)—C(24)*	120·3 (3)	121·0 (4)	122·4 (4)
C(23)—C(24)—C(25)*	120·0 (3)	117·8 (4)	118·8 (4)
C(23)—C(24)—C(27)*		121·1 (4)	
C(25)—C(24)—C(27)*		121·1 (4)	
C(24)—C(25)—C(26)*	120·7 (3)	122·4 (4)	118·3 (4)
C(21)—C(26)—C(25)*	118·3 (3)	118·8 (4)	120·1 (4)
C(24)—C(24a)—C(25)*			123·1 (4)
C(25)—C(24a)—C(28a)			118·0 (4)
C(24a)—C(25)—C(26)			121·4 (5)
C(25)—C(26)—C(27)			119·7 (5)
C(21)—C(28a)—C(24a)			118·3 (4)
C(21)—C(28a)—C(28)			122·3 (4)
C(24a)—C(28a)—C(28)			119·3 (4)

Table 2 (cont.)

|	(4a)	(4b)	(5)
O(3)–S–O(1)–C(11)	−34·7 (2)	−37·4 (3)	−29·0 (4)
O(4)–S–O(1)–C(11)*	−164·2 (2)	−166·8 (2)	−159·7 (3)
C(21)–S–O(1)–C(11)*	82·3 (2)	79·3 (3)	87·6 (3)
O(1)–S–C(21)–C(22)*	75·2 (3)	75·3 (3)	64·2 (4)
O(1)–S–C(21)–C(26)*	−107·5 (3)	−106·6 (3)	−118·7 (4)
O(3)–S–C(21)–C(22)*	−167·1 (3)	75·3 (3)	−178·4 (4)
O(3)–S–C(21)–C(26)*	10·2 (3)	11·2 (3)	−1·2 (5)
O(4)–S–C(21)–C(22)*	−35·4 (3)	−35·1 (3)	−45·8 (4)
O(4)–S–C(21)–C(26)*	142·0 (3)	143·0 (3)	131·4 (4)
S–O(1)–C(11)–C(12)	−142·3 (2)	−147·2 (2)	−139·6 (3)
S–O(1)–C(11)–C(16)	96·8 (3)	91·9 (3)	99·3 (4)
O(1)–C(11)–C(12)–O(2)	62·8 (3)	64·0 (3)	66·4 (4)
O(1)–C(11)–C(12)–C(13)	−175·7 (2)	−174·8 (3)	−174·4 (3)
C(16)–C(11)–C(12)–O(2)	−178·4 (3)	−176·5 (3)	−175·4 (4)
C(16)–C(11)–C(12)–C(13)	−56·9 (3)	−55·3 (4)	−56·3 (5)
O(1)–C(11)–C(16)–C(15)	174·7 (3)	173·1 (3)	174·2 (4)
C(12)–C(11)–C(16)–C(15)	57·1 (3)	56·2 (4)	57·6 (5)
O(2)–C(12)–C(13)–C(14)	179·2 (3)	178·0 (3)	176·0 (4)
C(11)–C(12)–C(13)–C(14)	56·5 (3)	55·5 (4)	55·1 (5)
C(12)–C(13)–C(14)–C(15)	−56·3 (3)	−56·5 (4)	−56·4 (6)
C(13)–C(14)–C(15)–C(16)	54·9 (3)	56·6 (4)	56·1 (6)
C(14)–C(15)–C(16)–C(11)	−55·4 (3)	−56·7 (4)	−56·5 (5)
S–C(21)–C(22)–C(23)*	176·6 (3)	177·4 (3)	175·2 (4)
S–C(21)–C(26)–C(25)*	−176·8 (3)	−177·6 (3)	−174·9 (4)

*C(21, 22, 23, 24, 25 and 26) become C(22, 23, 24, 24a, 28a and 21), respectively, in (5). Sign convention as defined by Klyne & Prelog (1960).

seems improbably short. [The corresponding contacts for (4b) are 3·01, 3·12, 2·37 and 1·65 Å, respectively.] It is thus possible that the hydroxyl H is disordered, the atom H(O2) being only one of two or more possible sites. In view of these problems, no great confidence should be placed in the reported position of H(O2).

The three sulfonate esters crystallize in closely similar conformations: Fig. 1(d) shows a superposition of (4a) and (4b), which are essentially isostructural. Not only are all the torsion angles in the three chair-cyclohexane rings within 2° of each other, and of those in the parent diol, but torsion angles within the sulfonate ester groups also vary very little between the three compounds. C(21)–S–O(1)–C(11) and S–O(1)–C(11)–C(16), for example, are 82·3 (2), 79·3 (3), 87·6 (3)° and 96·8 (3), 91·9 (3), 99·3 (4)°, respectively, for (4a), (4b) and (5). The O(2)–H bond is roughly antiperiplanar to C(12)–C(13) in each case. So the three structures together give us very precise parameters for what may be presumed to be the typical sulfonate ester structure of trans-cyclohexanediol in its ground-state conformation.

The two C—O bonds in the three sulfonate esters (4a), (4b) and (5) have very different lengths. C(11)—OSO₂Ar is lengthened to 1·476 (3), 1·476 (3) and 1·480 (6) Å, whereas C(12)—OH is the same length [1·428 (3), 1·425 (3), 1·427 (5) Å] as in the diol [1·429 (2) Å (Jones, Edwards & Kirby, 1989b)]. This is the usual effect on a C—OX bond of making the oxygen atom of a group OX more electron-withdrawing. This lengthening is described by a good linear relationship with the pK_a of HOX [correlation coefficient $r=0·986$ for eight data points, using the pK_a's given by Edwards, Jones & Kirby (1986) and the same pK_a's for benzene and naphthalenesulfonic acids as for p-toluenesulfonic
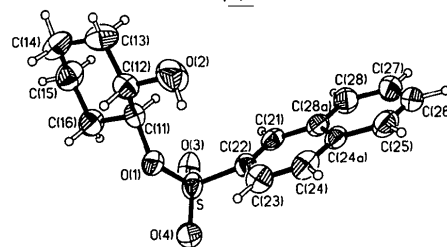
acid]. However the bond shows no extra lengthening which might be attributed to the involvement of the 2-OH group [C—O bond lengths are available for p-toluenesulfonates of several cyclohexanols: the one equatorial C—O bond length is 1·474 (2) Å (Johnson, Cheer, Schaefer, James & Moore, 1972) compared with a mean for three axial derivatives of 1·488 (11) Å
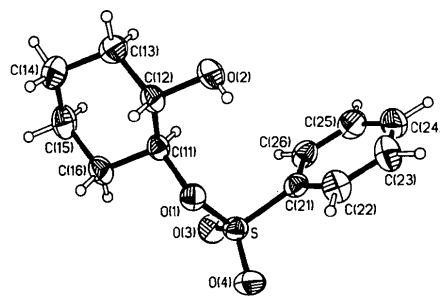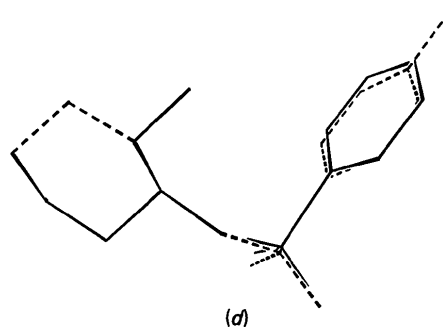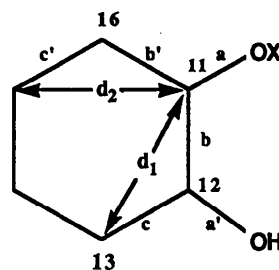

(a)
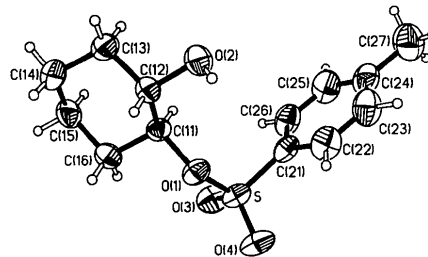
(b)

(c)

(d)

Fig. 1. (a) Molecular structure of (4a), showing the atom-numbering scheme. (b) Molecular structure of (4b), showing the atom-numbering scheme. (c) Molecular structure of (5), showing the atom-numbering scheme. (d) Superposition of (4a) and (4b), which are close to isostructural.

(James & Grainger, 1972; James, 1973; Johnson, Schaefer, James & Moore, 1972)].

The 1,2-shift leading to the pinacol rearrangement of these systems [(2)→(3)] involves the formation of a new bond between C(11) and C(13), as the σ-bonding electrons of the C(12)—C(13) bond overlap with the antibonding σ^*_{C-OX} orbital. The *trans* diequatorial conformation of this system provides the optimal, antiperiplanar geometry for this process, and we compare in Table 3 the key dihedral angles C(13)—C(12)—C(11)—O(1) and distances C(11)—C(13) (T_1 and d_1) across which the new bond must be made, with the corresponding dihedral angles C(15)—C(16)—C(11)—O(1) and distances C(11)—C(15) (T_2 and d_2) in the direction away from the OH group.

The first four entries in Table 3 show that the lengthening of the C—OX bond is accompanied by a significant decrease in the interatomic distance C(11)—C(13). This behaviour might indeed represent the early stages of the process which leads to the formation of a bond between the two centres. However, this process clearly goes no further as the leaving group is improved, in particular for the three sulfonate esters described in this paper. It cannot therefore be related to the rearrangement process. Most likely it reflects simply the modest increase in ring puckering observed on going
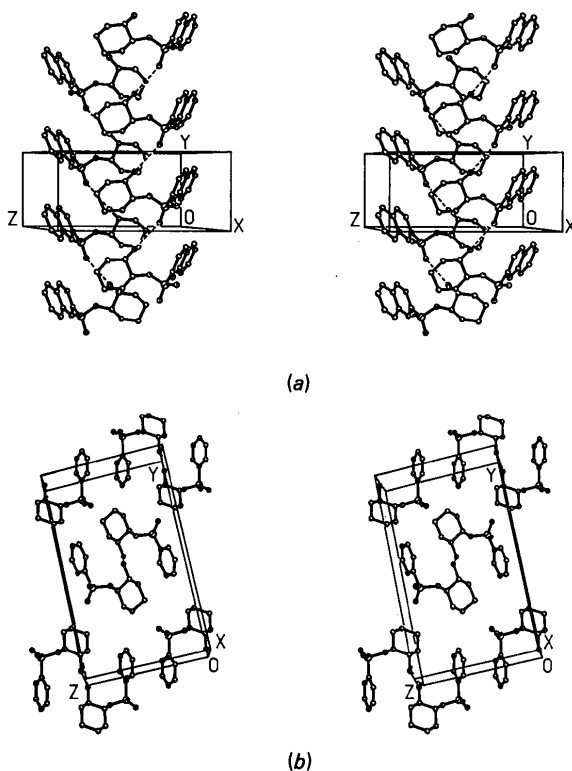

(a)

(b)

Fig. 2. (a) Molecular packing of (5), showing the pattern of hydrogen bonding. (b) Molecular packing of (4a), showing the putative pattern of hydrogen bonding.

Table 3. *Comparison of geometrical properties of the compounds in this series*

| | Interatomic distances (Å) | | | Torsion angles (°) | |
	a	d_1	d_2	T_1	T_2
(1), X = H	1·429 (2)	2·504 (5)	2·518 (5)	178·7 (2)	177·2 (2)
(1), X = Ph	1·437 (5)	2·487 (7)	2·500 (7)	179·1 (3)	176·9 (3)
	1·442 (5)	2·477 (7)	2·487 (7)	178·6 (3)	176·9 (3)
(1), X = pNP	1·466 (3)	2·466 (5)	2·490 (5)	179·5 (2)	176·2 (2)
(1), X = 2,4-DNB	1·473 (3)	2·478 (5)	2·492 (5)	176·0 (2)	173·7 (3)
(4a), R = H	1·476 (3)	2·469 (5)	2·501 (5)	175·7 (2)	174·7 (3)
(4b), R = Me	1·476 (3)	2·478 (5)	2·493 (5)	174·8 (3)	173·1 (3)
(5)	1·480 (6)	2·473 (9)	2·487 (9)	174·4 (3)	174·2 (4)

from (2), X = H to X = Ph and *p*-nitrobenzoyl, which is not continued for the four better leaving groups.

The clear-cut conclusion is that there is no evidence from the eight structures described in this series for any coupling of C—OX bond lengthening with geometrical changes at the adjacent C—OH centre. We observe no more than the changes associated with the early stages of the S_N1 cleavage of the C—OX bond, a systematic lengthening of the bond and a modest increase in the C(16)—C(11)—C(12) angle. We have seen similar but larger changes in a benzylic system (Edwards, Jones & Kirby, 1986). The absence of significant flattening at the C—OX centre is not unexpected: even in the much more reactive tetrahydropyranyl acetal system (Briggs, Glenn, Jones, Kirby & Ramaswamy, 1984), only a very modest degree of flattening appears at the acetal centre even for the best leaving groups.

References

Briggs, A. J., Glenn, R., Jones, P. G., Kirby, A. J. & Ramaswamy, P. (1984). *J. Am. Chem. Soc.* **106**, 6200–6207.
Clegg, W. (1981). *Acta Cryst.* **A37**, 22–28.
Edwards, M. R., Jones, P. G. & Kirby, A. J. (1986). *J. Am. Chem. Soc.* **108**, 7067—7073.
Edwards, M. R., Kirby, A. J., Raithby, P. R. & Jones, P. G. (1987). *Acta Cryst.* **C43**, 300–303.
James, V. J. (1973). *Cryst. Struct. Commun.* **2**, 205–208, 307–310.
James, V. J. & Grainger, C. T. (1972). *Cryst. Struct. Commun.* **2**, 111–114.
Johnson, P. L., Cheer, C. J., Schaefer, J. P., James, V. J. & Moore, F. H. (1972). *Tetrahedron*, **28**, 2893–2900.
Johnson, P. L., Schaefer, J. P., James, V. J. & Moore, F. H. (1972). *Tetrahedron*, **28**, 2901–2908.
Jones, P. G., Edwards, M. R. & Kirby, A. J. (1989a). *Acta Cryst.* **C45**, 244–246.

JONES, P. G., EDWARDS, M. R. & KIRBY, A. J. (1989b). Acta Cryst. C45, 247–249.

JONES, P. G., EDWARDS, M. R. & KIRBY, A. J. (1989c). Acta Cryst. C45, 249–252.

JONES, P. G. & KIRBY, A. J. (1979). J. Chem. Soc. Chem. Commun. pp. 288–289.

JONES, P. G. & KIRBY, A. J. (1982). J. Chem. Soc. Chem. Commun. pp. 1365–1366.

JONES, P. G. & KIRBY, A. J. (1984). J. Am. Chem. Soc. 106, 6200–6206.

JONES, P. G. & KIRBY, A. J. (1986). J. Chem. Soc. Chem. Commun. pp. 444–445.

KLYNE, W. & PRELOG, V. (1960). Experientia, 16, 521–523.

ROGERS, D. (1981). Acta Cryst. A37, 734–741.

SHELDRICK, G. M. (1986). SHELXTL. Program for solving, refining and displaying crystal structures. Nicolet Corp., Madison, Wisconsin, USA.

TRIMMELL, D., STOUT, E. I., DOANE, W. M., RUSSELL, C. R., BERINGER, V., SAUL, M. & VAN GESSEL, G. (1975). J. Org. Chem. 40, 1337–1339.

Adamantane* Inclusion Complexes with Thiourea and Selenourea

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Abstract. Trigonal, $R\bar{3}c$, $Z = 6$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $T = 300$ K. (I) $C_{10}H_{16}.3SC(NH_2)_2$, $M_r = 364.6$, $a = 16.187$ (7), $c = 12.578$ (7) Å, $V = 2854$ (4) Å^3, $D_x = 1.273$ g cm^{-3}, $\mu = 3.85$ cm^{-1}, $F(000) = 1176$, $R = 0.094$ for 621 independent reflections. (II) $C_{10}H_{16}.3SeC(NH_2)_2$, $M_r = 505.3$, $a = 16.548$ (11), $c = 12.830$ (5) Å, $V = 3043$ (5) Å^3, $D_x = 1.654$ g cm^{-3}, $\mu = 58.6$ cm^{-1}, $F(000) = 1500$, $R = 0.080$ for 511 independent reflections. Twofold disordered adamantane molecules are included in channels formed in the structure by molecules of the host linked through N—H$\cdots$S or N—H$\cdots$Se hydrogen bonds.

Introduction. The crystal structure of selenourea (Rutherford & Calvo, 1969) contains nine independent $SeC(NH_2)_2$ molecules, linked in three-molecule spiral chains by what appear to be hydrogen bonds. Hydrogen bonds involving Se seem to have a severely limited crystal chemistry, since only bonds in the closely related molecules N-phenyl-N'-benzylselenourea (Hope, 1965) and 2,4-diselenouracil (Shefter, James & Mautner, 1966) have been reported.

The three-molecule spiral chain also occurs in thiourea inclusion complexes, such as the cyclohexane adduct (Lenné, 1954). Van Bekkum, Remijnse & Wepster (1969) have reported a number of selenourea adducts which appeared to be isostructural with the thiourea complexes. Therefore it was felt that this would provide an opportunity to confirm the hydrogen-bonding capability of selenourea, and, at the same time, obtain improved molecular dimensions.

Adamantane was chosen as guest since, being rigid and highly symmetric, it was unlikely to be highly disordered. Also the crystal structure and molecular dimensions of adamantane were already available (Nordman & Schmitkons, 1965; Donohue & Goodman, 1967).

Experimental. The preparation of van Bekkum et al. (1969) was followed. Colorless trigonal prismatic crystals were used for diffraction measurements using a Picker FACS-I diffractometer with graphite monochromator in the $\theta/2\theta$ scan mode. (I) Crystal dimensions $0.20 \times 0.25 \times 0.10$ mm. Lattice parameters were determined using 21 reflections ($40 \le 2\theta \le 45°$). Three standard reflections were measured every 100 reflections; during the data collection their intensity decreased by 2%. A total of 736 independent reflections was measured with $2\theta \le 55°$, $0 \le h \le 18$, $0 \le k \le 17$, $0 \le l \le 16$ at 300 (2) K; of these 621 were used in the refinement $[I/\sigma(I) > 0.9]$. Absorption corrections were not applied. $R = 0.094$, $wR = 0.117$, $S = 2.43$ based on F, 33 variables, $w = (2.6 - 0.0032|F| + 0.00028|F|^2)^{-2}$, maximum $\Delta/\sigma = 0.17$ in the final least-squares cycle, $(\Delta\rho)_{max} = 0.76$ e Å^{-3} in the final difference map. (II) Crystal dimensions $0.10 \times 0.12 \times 0.20$ mm. Lattice parameters were determined using 21 reflections ($32 \le 2\theta \le 43°$). Three standard reflections were measured every 40 reflections; during the data collection their intensity decreased by 15% and the

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* IUPAC name: tricyclo[3.3.1.1^{3,7}]decane.