Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *CELDIM* (Enraf–Nonius, 1988). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1253). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis- and *trans*-4-*tert*-Butylcyclohexyl *p*-Nitrobenzenesulfonate at 130 K

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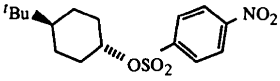
Abstract

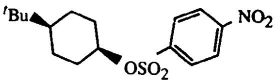
The structures of the title axial and equatorial cyclohexyl *p*-nitrobenzenesulfonate esters, $C_{16}H_{23}NO_5S$, determined at 130 K are reported. The $C_{alkyl}—O_{ester}$ bond distances of 1.487 (2) and 1.492 (2) Å are not significantly different from one another. The geometry of the sulfonate function with respect to both the phenyl and cyclohexane rings is essentially identical in both structures.

Comment

As part of our structural studies on the factors influencing C—O bond distances (White & Robertson, 1992; White, Green & Kuan, 1995), we required accurate C—O bond distances for axial and equatorial cyclohexyl *p*-nitrobenzenesulphonate esters for comparison purposes. The conformationally constrained cyclohexyl nosylates, *trans*-4-*tert*-butylcyclohexyl *p*-nitrobenzenesulfonate, (1), and *cis*-4-*tert*-butylcyclohexyl *p*-nitrobenzenesulfonate, (2), were chosen for this low-temperature study.

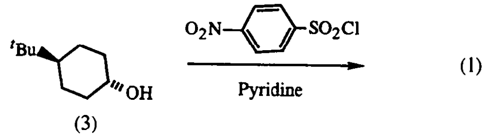


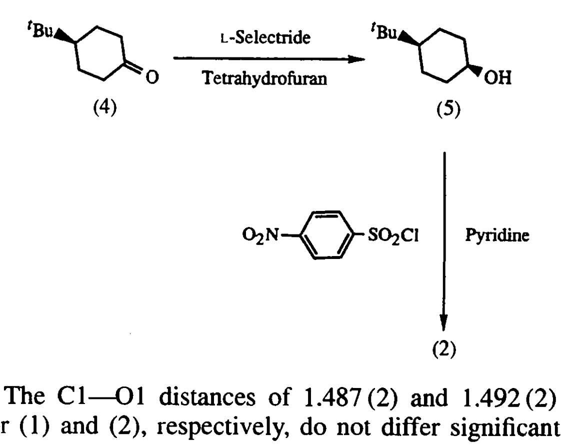
(1)



(2)

Compound (1) was prepared by esterification of commercially available *trans*-4-*tert*-butylcyclohexanol, (3), with *p*-nitrobenzenesulfonyl chloride in pyridine, and (2) was prepared by selective reduction of 4-*tert*-butylcyclohexanone, (4), with L-selectride giving *cis*-4-*tert*-butylcyclohexanol, (5), as the major product, which was similarly esterified using *p*-nitrobenzenesulfonyl chloride in pyridine.





The C1—O1 distances of 1.487 (2) and 1.492 (2) Å for (1) and (2), respectively, do not differ significantly from one another. The geometry about the sulfonate ester function is essentially identical in both structures; the S—O2 bond is close to being eclipsed with the aromatic ring, the S—O3 and S—O1 bonds are approximately equally above and below the plane of the phenyl ring, and the O3—S—O1 bond angle is bisected by the C11—C16 bond. Furthermore, the geometrical relationship of the sulfonate ester with respect to the C1, C2 and C3 atoms of the cyclohexane ring, as defined by the dihedral angles about the C1—O1 and O1—S bonds, is very similar for both structures.

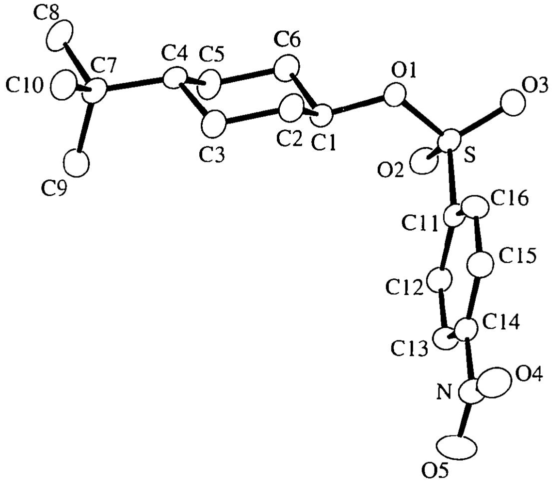


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of (1). Displacement ellipsoids are at the 50% probability level and H atoms have been omitted.

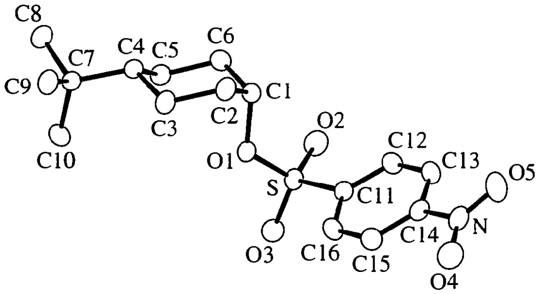


Fig. 2. *ORTEP*II (Johnson, 1976) diagram of (2). Displacement ellipsoids are at the 50% probability level and H atoms have been omitted.

Experimental

Rock-like crystals of (1) (m.p. 363–364 K) were grown from methanol, while plate-like crystals of (2) (m.p. 382–383 K) were grown from petroleum. The temperature of the crystals was maintained at 130 K during data collection using an Oxford Cryostream cooling device.

Compound (1) (*trans*)

Crystal data

$C_{16}H_{23}NO_5S$
$M_r = 341.43$
Monoclinic
$P2_1/c$
$a = 12.603\ (3)$ Å
$b = 9.5200\ (10)$ Å
$c = 14.762\ (5)$ Å
$\beta = 107.81\ (2)°$
$V = 1686.2\ (7)$ Å^3
$Z = 4$
$D_x = 1.345$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12–16°$
$\mu = 0.216$ mm^{-1}
$T = 130.0\ (1)$ K
Block
0.4 × 0.4 × 0.3 mm
Colourless

Data collection

Enraf–Nonius CAD-4-Machs diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5083 measured reflections
4298 independent reflections
3738 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0152$
$\theta_{\rm max} = 29.96°$
$h = -17 \rightarrow 16$
$k = -13 \rightarrow 12$
$l = -15 \rightarrow 20$
3 standard reflections
frequency: 160 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0379$
$wR(F^2) = 0.1064$
$S = 1.041$
4297 reflections
301 parameters
H-atom coordinates and isotropic displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.7912P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.580$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.280$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0009 (8)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S	0.01521 (3)	0.07762 (3)	0.69143 (2)	0.02231 (10)
N	0.24175 (10)	0.15447 (13)	1.10649 (8)	0.0273 (3)
O1	0.05930 (8)	−0.06790 (10)	0.67025 (7)	0.0245 (2)
O2	0.04891 (9)	0.18726 (10)	0.64000 (7)	0.0271 (2)
O3	−0.10058 (9)	0.05557 (12)	0.67847 (8)	0.0305 (2)
O4	0.22089 (11)	0.06932 (12)	1.16072 (8)	0.0361 (3)
O5	0.30432 (11)	0.25483 (13)	1.13208 (8)	0.0411 (3)
C1	0.17520 (11)	−0.07504 (13)	0.66514 (10)	0.0214 (3)
C2	0.22770 (13)	−0.20570 (15)	0.71820 (10)	0.0255 (3)
C3	0.34521 (12)	−0.2248 (2)	0.70980 (10)	0.0251 (3)
C4	0.34479 (11)	−0.23086 (13)	0.60629 (9)	0.0214 (3)
C5	0.28661 (12)	−0.0994 (2)	0.55342 (10)	0.0263 (3)
C6	0.16938 (12)	−0.0809 (2)	0.56145 (10)	0.0259 (3)
C7	0.46166 (12)	−0.25428 (14)	0.59438 (10)	0.0248 (3)
C8	0.4502 (2)	−0.2793 (2)	0.48906 (12)	0.0364 (4)
C9	0.53932 (13)	−0.1284 (2)	0.63037 (13)	0.0321 (3)
C10	0.51647 (14)	−0.3848 (2)	0.65012 (12)	0.0329 (3)
C11	0.08530 (11)	0.10156 (13)	0.81398 (9)	0.0211 (3)
C12	0.15278 (12)	0.21783 (14)	0.84457 (10)	0.0238 (3)

C13	0.20440 (12)	0.23575 (14)	0.94176 (10)	0.0245 (3)
C14	0.18724 (11)	0.13626 (14)	1.00351 (9)	0.0223 (3)
C15	0.12088 (12)	0.01873 (15)	0.97358 (10)	0.0254 (3)
C16	0.06844 (12)	0.00178 (15)	0.87712 (10)	0.0256 (3)

Table 2. *Selected geometric parameters (Å, °) for (1)*

S—O3	1.4281 (11)	S—C11	1.7684 (15)
S—O2	1.4295 (11)	O1—C1	1.487 (2)
S—O1	1.5595 (10)		
O3—S—O2	119.58 (7)	O1—S—C11	102.85 (6)
O3—S—O1	104.75 (6)	C1—O1—S	117.81 (8)
O2—S—O1	111.11 (6)	O1—C1—C2	107.01 (11)
O3—S—C11	109.04 (7)	O1—C1—C6	108.00 (11)
O2—S—C11	108.22 (7)		
O3—S—O1—C1	172.00 (9)	O3—S—C11—C12	−127.52 (11)
O2—S—O1—C1	41.54 (11)	O2—S—C11—C12	4.03 (13)
C11—S—O1—C1	−74.05 (10)	O1—S—C11—C12	121.68 (11)
S—O1—C1—C2	136.90 (10)	O3—S—C11—C16	51.40 (12)
S—O1—C1—C6	−102.47 (11)	O2—S—C11—C16	−177.05 (10)
O1—C1—C2—C3	176.14 (11)	O1—S—C11—C16	−59.40 (12)

Compound (2) (*cis*)

Crystal data

$C_{16}H_{23}NO_5S$
$M_r = 341.43$
Monoclinic
$P2_1$
$a = 6.612$ (2) Å
$b = 9.333$ (2) Å
$c = 13.819$ (3) Å
$\beta = 96.72$ (3)°
$V = 846.8$ (4) Å^3
$Z = 2$
$D_x = 1.339$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ (nickel filtered) radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 20$–35°
$\mu = 1.917$ mm^{-1}
$T = 130.0$ (1) K
Plate
0.49 × 0.24 × 0.04 mm
Colourless

Data collection

Enraf–Nonius CAD-4-Machs diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (*SHELX76*; Sheldrick, 1976)
$T_{\min} = 0.57$, $T_{\max} = 0.93$
3814 measured reflections
3409 independent reflections

3314 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0545$
$\theta_{\max} = 74.82°$
$h = -7 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -1 \rightarrow 17$
3 standard reflections
frequency: 160 min
intensity decay: 2.5%

Refinement

Refinement on F^2
$R(F) = 0.0408$
$wR(F^2) = 0.1755$
$S = 0.837$
3379 reflections
301 parameters
H-atom coordinates and isotropic displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1293P)^2 + 0.1708P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.157$

$\Delta\rho_{\max} = 0.428$ e Å^{-3}
$\Delta\rho_{\min} = -0.644$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0017 (10)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.00 (2)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S	0.30538 (7)	0.07115 (5)	0.85303 (3)	0.0241 (2)
N	1.1037 (3)	0.1291 (2)	1.09847 (14)	0.0298 (4)
O1	0.3665 (2)	0.0054 (2)	0.75672 (11)	0.0254 (3)
O2	0.1802 (3)	−0.0256 (2)	0.89913 (12)	0.0320 (4)
O3	0.2338 (3)	0.2114 (2)	0.82619 (12)	0.0323 (4)
O4	1.2159 (3)	0.2257 (2)	1.07889 (14)	0.0413 (4)
O5	1.1480 (3)	0.0389 (2)	1.16194 (13)	0.0435 (5)
C1	0.4159 (4)	−0.1504 (2)	0.75420 (15)	0.0265 (4)
C2	0.5895 (3)	−0.1600 (3)	0.6921 (2)	0.0297 (5)
C3	0.5268 (3)	−0.1124 (3)	0.5869 (2)	0.0279 (4)
C4	0.3382 (3)	−0.1924 (2)	0.53878 (15)	0.0240 (4)
C5	0.1656 (3)	−0.1778 (2)	0.6035 (2)	0.0260 (4)
C6	0.2276 (4)	−0.2283 (2)	0.7079 (2)	0.0289 (5)
C7	0.2711 (4)	−0.1477 (2)	0.43095 (15)	0.0263 (4)
C8	0.1193 (4)	−0.2577 (3)	0.3824 (2)	0.0374 (5)
C9	0.4563 (4)	−0.1440 (3)	0.3731 (2)	0.0358 (5)
C10	0.1706 (4)	−0.0001 (3)	0.4242 (2)	0.0328 (5)
C11	0.5397 (3)	0.0888 (2)	0.92774 (13)	0.0224 (4)
C12	0.5792 (4)	0.0058 (2)	1.0112 (2)	0.0270 (4)
C13	0.7636 (4)	0.0201 (2)	1.0687 (2)	0.0273 (4)
C14	0.9014 (3)	0.1183 (2)	1.04093 (14)	0.0235 (4)
C15	0.8630 (4)	0.2044 (2)	0.9592 (2)	0.0274 (4)
C16	0.6800 (4)	0.1887 (2)	0.9011 (2)	0.0273 (4)

Table 4. *Selected geometric parameters (Å, °) for (2)*

S—O1	1.561 (2)	S—C11	1.766 (2)
S—O2	1.425 (2)	O1—C1	1.492 (2)
S—O3	1.426 (2)		
O2—S—O3	120.37 (11)	O1—S—C11	103.78 (9)
O2—S—O1	110.74 (9)	C1—O1—S	118.84 (13)
O3—S—O1	104.50 (9)	O1—C1—C6	107.8 (2)
O2—S—C11	108.28 (10)	O1—C1—C2	104.6 (2)
O3—S—C11	107.93 (10)		
O2—S—O1—C1	−38.8 (2)	O2—S—C11—C12	4.8 (2)
O3—S—O1—C1	−169.9 (2)	O3—S—C11—C12	136.6 (2)
C11—S—O1—C1	77.1 (2)	O1—S—C11—C12	−112.9 (2)
S—O1—C1—C6	98.2 (2)	O2—S—C11—C16	−174.4 (2)
S—O1—C1—C2	−142.62 (14)	O3—S—C11—C16	−42.6 (2)
O1—C1—C2—C3	−63.9 (2)	O1—S—C11—C16	67.9 (2)

The structures were both solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Refinement was performed using *SHELXL*93 (Sheldrick, 1993) with anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for H atoms. The figures were drawn using *ORTEP*II (Johnson, 1976) and the tables prepared using *SHELXL*93. All calculations were carried out on a VAXstation 4000VLC computer system.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 3207–3210

Stereochemistry of Chiral Sulfoxides used for the Synthesis of Antitumor Antibiotic Analogues of Sparsomycin

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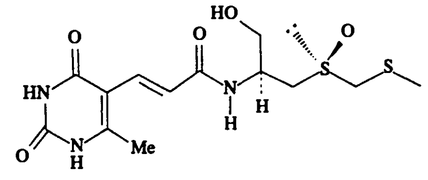
Abstract

The structures of {[(*S*)-(4,5-dihydro-2-phenyloxazol-4-yl)-methyl]-(*S*)-sulfinyl}octane, $C_{18}H_{27}NO_2S$, (2), {[(*S*)-(4,5-dihydro-2-phenyloxazol-4-yl)methyl]-(*R*)-sulfinyl}octane, $C_{18}H_{27}NO_2S$, (3), and 4-{[(*S*)-(4,5-dihydro-2-phenyloxazol-4-yl)methyl]-(*S*)-sulfinyl}phenol, $C_{16}H_{15}NO_3S$, (5), have been determined. The known chirality (*S*) at the C10 atom in all three compounds enabled assignment of the absolute configuration at the S13 atom. The C10 chirality was subsequently confirmed by refinement of the Flack parameter. The absolute configuration at S13 for compounds (2), (3) and (5) is *R*, *S* and *S*, respectively. Comparison with the stereochemistry of sparsomycin enables proper choice of diastereomers for analogue development.

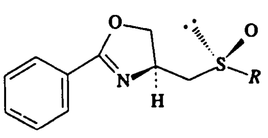
Comment

Sparsomycin, (1), a natural product from bacteria, is a potent inhibitor of protein biosynthesis (Lazaro, San Felix, van den Broek, Ottenheijm & Ballesta, 1991) and has attracted considerable interest as an antibiotic and chemotherapeutic agent (Ottenheijm, van den Broek, Ballesta & Zylicz, 1986). The drug preferentially binds to 'active ribosomes' engaged in polypeptide synthesis on mRNA and blocks the action of peptidyl transferase, a key enzyme which is an integral part of the large ribosomal subunit structure. Valuable information on the structure of this peptidyl transferase centre and of the ribosome as a whole has been obtained from studies using sparsomycin and its analogues.

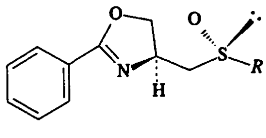
In connection with our syntheses of ribosome inhibitors based on the structure of sparsomycin, we have prepared a novel pair of optically active alkyl *n*-octyl sulfoxides, (2) and (3), and report on their solid-state structures. Curiously, the diastereomeric octyl sulfoxides (2) and (3) can be separated on silica gel, but the related alkyl aryl sulfoxide diastereomers (4) and (5) could not be separated except by selective and repeated crystallizations. We also report on the solid-state structure of compound (5). We have relied on X-ray crystallography for determining the chirality of these sulfoxide centres, since there are no other general methods for compounds that also contain other chiral centres.



(1)



(2) R = *n*-octyl
(4) R = *p*-(HO)-Ph



(3) R = *n*-octyl
(5) R = *p*-(HO)-Ph

The molecular structures of the three compounds investigated are presented in Figs. 1, 2 and 3. Compound (2) (Fig. 1) contains two independent molecules in the asymmetric unit, both having the same stereochemistry. The *n*-octyl chains in both molecules of compound (2) and in compound (3) (Fig. 2) all adopt fully extended conformations.

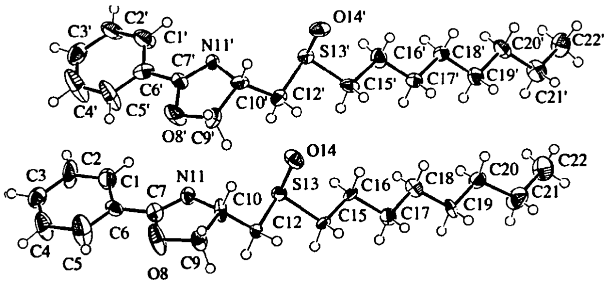


Fig. 1. The structure of (2) showing 50% probability displacement ellipsoids (two independent molecules in the asymmetric unit).