

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: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (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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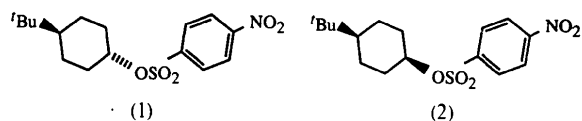
Abstract

The structures of the title axial and equatorial cyclohexyl *p*-nitrobenzenesulfonate esters, C₁₆H₂₃NO₅S, de-

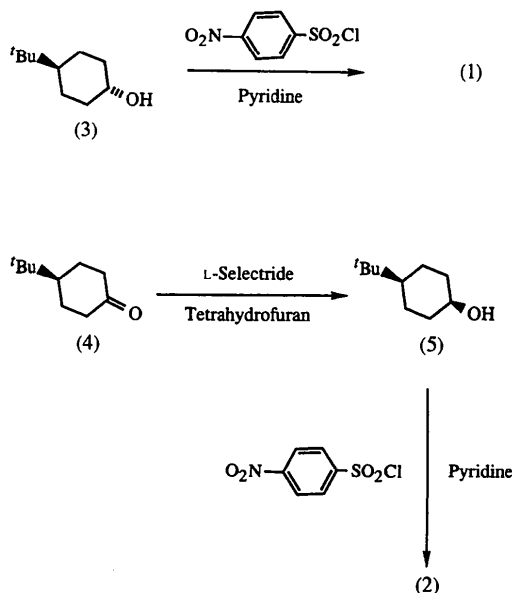
termined at 130 K are reported. The C_{alkyl}—O_{ester} bond distances of 1.487 (2) and 1.492 (2) Å are not significantly different from one another. The geometry of the sulfonate function with respect to both the phenyl and cyclohexane rings is essentially identical in both structures.

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.



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.

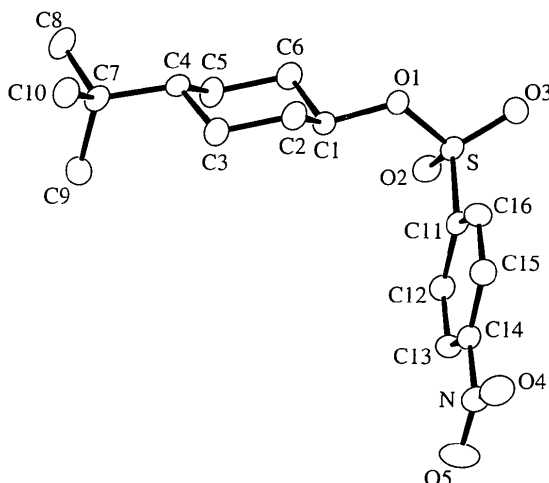


Fig. 1. ORTEP (Johnson, 1976) diagram of (1). Displacement ellipsoids are at the 50% probability level and H atoms have been omitted.

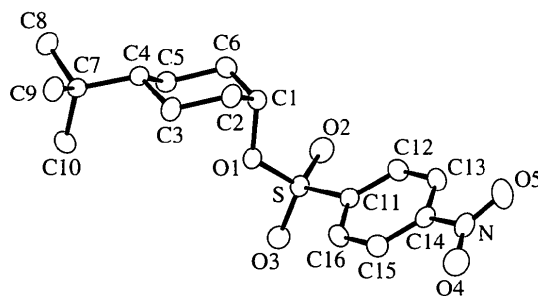


Fig. 2. ORTEP (Johnson, 1976) diagram of (2). Displacement ellipsoids are at the 50% probability level and H atoms have been omitted.

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
 $P2_1/c$
 $a = 12.603(3) \text{ \AA}$
 $b = 9.5200(10) \text{ \AA}$
 $c = 14.762(5) \text{ \AA}$
 $\beta = 107.81(2)^\circ$
 $V = 1686.2(7) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.345 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

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

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 $P = (F_o^2 + 2F_c^2)/3$

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

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

$(\Delta/\sigma)_{max} = 0.005$
 $\Delta\rho_{max} = 0.580 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.280 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL93* (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 ($\text{\AA}^2$) for (1)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{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 ($\text{\AA}$, $^\circ$) 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*C₁₆H₂₃NO₅S $M_r = 341.43$

Monoclinic

 $P2_1$ $a = 6.612$ (2) $\text{\AA}$ $b = 9.333$ (2) $\text{\AA}$ $c = 13.819$ (3) $\text{\AA}$ $\beta = 96.72$ (3) $^\circ$ $V = 846.8$ (4) $\text{\AA}^3$ $Z = 2$ $D_x = 1.339$ Mg m⁻³ D_m not measured*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

Cu $K\alpha$ (nickel filtered) radiation $\lambda = 1.5418$ $\text{\AA}$

Cell parameters from 25 reflections

 $\theta = 20\text{--}35^\circ$ $\mu = 1.917$ mm⁻¹ $T = 130.0$ (1) K

Plate

 $0.49 \times 0.24 \times 0.04$ mm

Colourless

3314 observed reflections [$I > 2\sigma(I)$] $R_{\text{int}} = 0.0545$ $\theta_{\max} = 74.82^\circ$ $h = -7 \rightarrow 8$ $k = -11 \rightarrow 11$ $l = -1 \rightarrow 17$

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 $\text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.644$ e $\text{\AA}^{-3}$

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 ($\text{\AA}^2$) for (2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{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 ($\text{\AA}$, $^\circ$) 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 SHELXS86 (Sheldrick, 1985). Refinement was performed using SHELXL93 (Sheldrick, 1993) with anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for H atoms. The figures were drawn using ORTEPII (Johnson, 1976) and the tables prepared using SHELXL93. 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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Stereochemistry of Chiral Sulfoxides used for the Synthesis of Antitumor Antibiotic Analogues of Sparsomycin

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Abstract

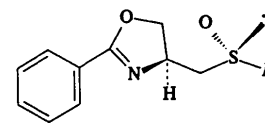
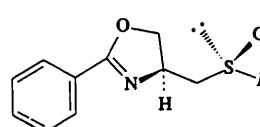
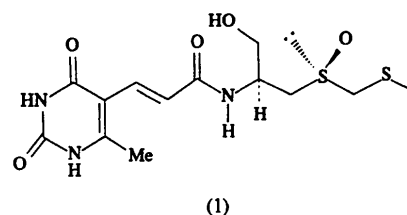
The structures of {[*(S)*-(4,5-dihydro-2-phenyloxazol-4-yl)methyl]-(*S*)-sulfinyl}octane, C₁₈H₂₇NO₂S, (2), {[*(S)*-(4,5-dihydro-2-phenyloxazol-4-yl)methyl]-(*R*)-sulfinyl}octane, C₁₈H₂₇NO₂S, (3), and 4-[[*(S)*-(4,5-dihydro-2-phenyloxazol-4-yl)methyl]-(*S*)-sulfinyl]phenol, C₁₆H₁₅NO₃S, (5), have been 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.



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.

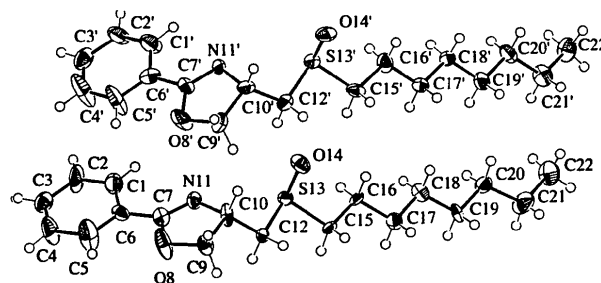


Fig. 1. The structure of (2) showing 50% probability displacement ellipsoids (two independent molecules in the asymmetric unit).