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(*R*)-2-Hydroxy-3-iodo-2-methylpropyl 4-Nitrobenzenesulfonate

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Abstract

The global minimum conformation, as computed by *PCMODEL* [Gajewski & Gilbert (1992). Serena Software, Bloomington, IN, USA], of the title compound agrees with that observed in the crystal. In the crystal, the torsion angles I—CH$_2$—C—CH$_2$O, ICH$_2$—C—CH$_2$—O, C—CH$_2$—O—S and CH$_2$—O—S—C are −57.7 (4), −61.7 (4), 171.2 (2) and −73.0 (3)°, respectively. Weak intermolecular hydrogen bonding connects $O_{O—H}$ and $O_{S=O}$ with an O···O distance of 2.927 (4) Å and an angle about the H atom of 165 (4)°.

Comment

As part of an effort to synthesize chiral enzyme inhibitors, we prepared the title compound by reaction of (*S*)-(1-methyloxiranyl)methyl 4-nitrobenzenesulfonate with sodium iodide in acetic acid at 273 K. We undertook the determination of the solid-state conformation of the title compound so as to compare it to those conformations predicted in molecular modeling studies.

PCMODEL (Gajewski & Gilbert, 1992) was used to calculate the 81 possible staggered conformations of the four-torsion-angle sequence IC—C—C—O—SO$_2$Ar (where Ar is the aryl ring). For the global minimum these torsion angles are −58.9, −55.2, 169.3 and −83.6°, respectively. In the crystal they are −57.7 (4), −61.7 (4), 171.2 (2) and −73.0 (3)°, respectively. In this conformation, the I atom is on top of the benzene ring with nearly equal distances between the I atom and six C atoms of the benzene ring. The intramolecular distance [4.083 (2) Å] between I and the centroid of the aryl ring is almost equal to the sum (3.90 Å) of the van der Waals radius of I and the thickness of the benzene ring (Wheland, 1960).

With respect to bond distances and angles, *PCMODEL* agrees approximately with the X-ray determination. Notable exceptions are the C1—C2, C7—C8 and C8—C9 bond lengths and the C7—C8—C9 and O5—N—O6 bond angles, as well as many values of the SO$_3$ group. The X-ray results reveal that the O2—C3 bond is 0.049 Å longer than the O1—C2 bond, which is consistent with OSO$_2$Ar being a better leaving group than the OH group (Allen & Kirby, 1984; Jones, Dölle, Kirby & Parker, 1992; Jones, Kirby & Parker, 1992; Jones, Schmidt-Bäse, Edwards & Kirby, 1992; Kirby, Parker & Raithby, 1992). Molecules are linked in chains along **b** by weak intermolecular hydrogen bonds involving $O_{O—H}$ and $O_{S=O}$. The O1···O3 distance is 2.927 (4) Å and the O···H—O angle is 165 (4)°.

A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) reveals one related structure, 7-*exo*-isopropenylbicyclo[4.1.0]hept-7-

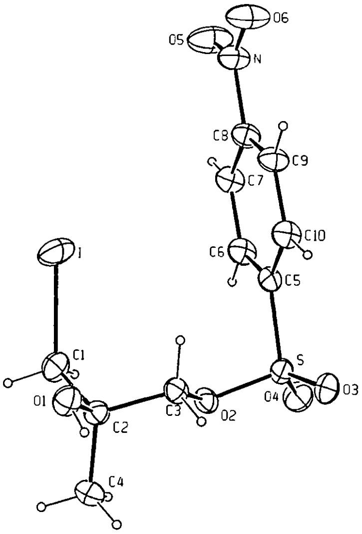

Fig. 1. Numbering scheme with thermal ellipsoids drawn at the 30% probability level. H atoms are drawn as circles of arbitrary radii.

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endo-yl 4-nitrobenzenesulfonate (Seebach, Dammann, Lindner & Kitschke, 1979). Other related structures are (*R*)-(1-methyloxiranyl)methyl 4-nitrobenzenesulfonate (Sun, Fronczek & Gandour, 1992), 2-fluoro-2-phenylethyl 4-nitrobenzenesulfonate (Jones, Dölle, Kirby & Parker, 1992), 2-fluoroethyl 4-nitrobenzenesulfonate and 2,2,2-trifluoroethyl 4-nitrobenzenesulfonate (Jones, Kirby & Parker, 1992).

Experimental

Crystal data

$C_{10}H_{12}INO_6S$
$M_r = 401.2$
Orthorhombic
$P2_12_12_1$
$a = 7.6958$ (4) Å
$b = 9.4503$ (6) Å
$c = 19.4832$ (8) Å
$V = 1417.0$ (2) Å^3
$Z = 4$
$D_x = 1.880$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11-13°$
$\mu = 2.4$ mm^{-1}
$T = 300$ K
Elongated octahedron
0.45 × 0.38 × 0.30 mm
Colourless
Crystal source: crystallized from methanol

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{\min} = 0.880$, $T_{\max} = 0.999$
2819 measured reflections
2791 independent reflections
2304 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 32°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 28$
3 standard reflections
frequency: 167 min
intensity variation: <1%

Refinement

Refinement on F
Final $R = 0.032$
$wR = 0.040$
$S = 2.139$
2304 reflections
177 parameters
$w = 4F^2[\sigma^2(I) + (0.02F^2)^2]^{-1}$
$(\Delta/\sigma)_{\max} = 0.07$
$\Delta\rho_{\max} = 0.79$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: $(1 + gI_c)^{-1}$ applied to F_c
Extinction coefficient: $g = 1.3$ (2) × 10^{-7}
Atomic scattering factors from Cromer (1974) and Cromer & Waber (1974)

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

$$B_{\rm eq} = \frac{8\pi^2}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
I	0.45279 (4)	0.20426 (4)	0.58898 (2)	5.197 (6)
S	1.0201 (1)	0.4066 (1)	0.64956 (5)	2.96 (2)
O1	0.6812 (4)	−0.0335 (3)	0.6731 (1)	3.70 (6)
O2	0.9623 (4)	0.2571 (3)	0.6228 (1)	2.89 (4)
O3	1.0675 (4)	0.3935 (3)	0.7199 (1)	4.11 (6)
O4	1.1438 (4)	0.4564 (4)	0.6003 (2)	4.35 (6)
O5	0.3280 (5)	0.7812 (4)	0.5697 (2)	6.31 (8)
O6	0.2808 (5)	0.7562 (4)	0.6774 (2)	5.66 (8)
N	0.3670 (5)	0.7379 (4)	0.6260 (2)	4.02 (7)
C1	0.6814 (6)	0.0809 (5)	0.5667 (2)	3.64 (8)
C2	0.7899 (5)	0.0432 (4)	0.6278 (2)	2.85 (6)
C3	0.8527 (5)	0.1716 (4)	0.6681 (2)	2.88 (6)
C4	0.9435 (6)	−0.0448 (5)	0.6034 (2)	4.19 (8)
C5	0.8302 (5)	0.5071 (4)	0.6441 (2)	2.70 (6)
C6	0.7812 (6)	0.5591 (5)	0.5802 (2)	3.36 (7)
C7	0.6270 (6)	0.6344 (4)	0.5743 (2)	3.38 (7)
C8	0.5292 (5)	0.6560 (4)	0.6324 (2)	3.06 (7)
C9	0.5740 (6)	0.6044 (5)	0.6961 (2)	3.36 (7)
C10	0.7292 (6)	0.5298 (5)	0.7024 (2)	3.27 (7)

Table 2. *Geometric parameters* (Å, °)

I—C5	4.217 (4)	O2—C3	1.464 (4)
I—C6	4.203 (4)	O5—N	1.209 (5)
I—C7	4.290 (4)	O6—N	1.214 (5)
I—C8	4.392 (4)	N—C8	1.474 (6)
I—C9	4.419 (4)	C1—C2	1.496 (5)
I—C10	4.344 (4)	C2—C3	1.523 (5)
I—C1	2.155 (4)	C2—C4	1.521 (6)
S—O2	1.570 (3)	C5—C6	1.392 (5)
S—O3	1.423 (3)	C5—C10	1.392 (5)
S—O4	1.432 (3)	C6—C7	1.388 (6)
S—C5	1.746 (4)	C7—C8	1.375 (5)
O1—C2	1.415 (5)	C8—C9	1.377 (5)
O1—H10H	0.71 (4)	C9—C10	1.392 (6)
O2—S—O3	108.3 (2)	C1—C2—C3	113.4 (3)
O2—S—O4	105.2 (2)	C1—C2—C4	108.4 (3)
O2—S—C5	103.4 (2)	C3—C2—C4	110.5 (3)
O3—S—O4	120.3 (2)	O2—C3—C2	108.2 (3)
O3—S—C5	108.7 (2)	S—C5—C6	118.2 (3)
O4—S—C5	109.7 (2)	S—C5—C10	120.1 (3)
C2—O1—H10H	95 (3)	C6—C5—C10	121.6 (4)
S—O2—C3	117.4 (2)	C5—C6—C7	119.1 (3)
O5—N—O6	124.4 (4)	C6—C7—C8	118.4 (3)
O5—N—C8	117.7 (4)	N—C8—C7	118.1 (3)
O6—N—C8	117.9 (3)	N—C8—C9	118.3 (3)
I—C1—C2	115.1 (3)	C7—C8—C9	123.5 (4)
O1—C2—C1	106.7 (3)	C8—C9—C10	118.3 (3)
O1—C2—C3	105.9 (3)	C5—C10—C9	119.0 (3)
O1—C2—C4	111.9 (3)		
C5—S—O2—C3	−73.0 (3)	S—O2—C3—C2	171.2 (2)
I—C1—C2—C3	−57.7 (4)	C1—C2—C3—O2	−61.7 (4)
O2—S—C5—C6	−78.8 (3)	H10H—O1—C2—C3	−73 (3)

The H atoms were located by difference Fourier synthesis. The H atom of the hydroxy group was refined isotropically, while the other H atoms were placed in calculated positions with a C—H bond length of 0.95 Å and $B_{\rm iso} = 1.3\,B_{\rm eq}$ of the bonded C atom. The absolute configuration, confirmed by the refinement of the inversion-related structure under identical conditions, was that expected from the configuration of the starting material. This refinement of the *S* isomer led to $R = 0.039$, $wR = 0.050$ and $S = 2.645$. The Enraf–Nonius *SDP* programs (Frenz & Okaya, 1980) were used.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55995 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1041]

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Structure of an Optically Active Anthracycline Precursor

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Abstract

The crystal structure of (1*S*,3*S*)-3-acetyl-5-methoxy-3-methylthio-1,2,3,4-tetrahydronaphthalene-1,8-diyl dibenzoate contains two independent molecules. These molecules have a similar conformation except for the dihedral angles between the aromatic ring and the benzoyloxy group linked to it, which differ by a relative rotation of −160°. The absolute configurations of the two chiral centres C8 and C10 are established as *S* and *S*.

Comment

The compound was synthesized as a precursor of optically pure anthracyclines. The structure determination of the compound was undertaken to confirm the absolute configurations of the two chiral centres, which were established as *S* and *S*. The C10 chiral centre was constructed *via* chirality-transferred ene reaction (Tanino, Shoda, Nakamura & Kuwajima, 1992), and the cyclohexane ring cyclization reaction between C7 and C8 afforded a single diastereomer. Details of the synthetic work will be published elsewhere (Adachi, Masuya, Tanino & Kuwajima, 1993).

The structure contains two independent $C_{28}H_{26}O_6S$ molecules which have similar conformations. The cyclohexane ring in each molecule adopts a half-chair conformation with an axial acetyl group and an equatorial methylthio group. The benzoyloxy group linked to the cyclohexane ring at C10 is in an equatorial position. The main difference between the two molecules is in the conformation of the benzoyloxy group at C2. The dihedral angles C1*A*—C2*A*—O3*A*—C15*A* and C1*B*—C2*B*—O3*B*—C15*B* are 84.8 (4) and −115.2 (4)°, respectively.

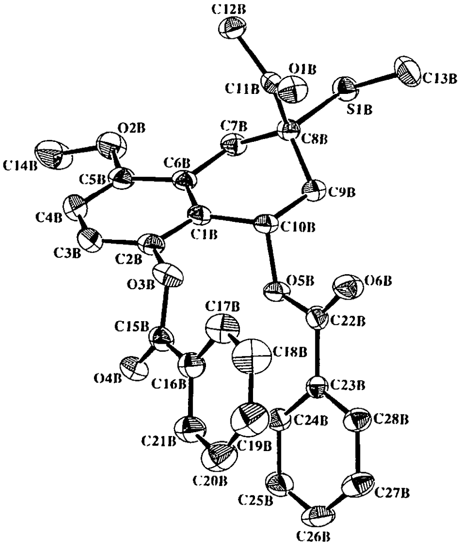

Fig. 1. A perspective view of molecule *B* with numbering scheme, excluding H atoms (30% probability ellipsoids).

Experimental

Crystal data

$C_{28}H_{26}O_6S$
M_r = 490.570
Triclinic
$P1$
a = 10.159 (2) Å
b = 13.533 (5) Å
c = 10.016 (3) Å
α = 108.10 (2)°
β = 102.92 (2)°
γ = 96.30 (2)°
V = 1251.5 (7) Å^3
Z = 2
D_x = 1.302 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 27.33–27.45°
μ = 1.447 mm^{-1}
T = 296.15 K
Prism
0.80 × 0.35 × 0.30 mm
Colourless
Crystal source: recrystallization from ethanol

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