216 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1214P)^2 + 0.0307P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.094$
$\Delta\rho_{\max} = 0.290$ e Å^{-3}
$\Delta\rho_{\min} = -0.237$ e Å^{-3}
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)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^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	0.92832 (10)	0.51629 (9)	0.86263 (3)	0.0538 (3)
O1	0.8354 (5)	0.6597 (3)	0.88601 (11)	0.0825 (9)
O2	0.8600 (2)	0.3954 (3)	0.70150 (8)	0.0474 (5)
O3	0.6470 (3)	0.5830 (3)	0.68440 (9)	0.0577 (6)
C1	0.8600 (4)	0.3407 (4)	0.90273 (12)	0.0455 (6)
C2	0.7631 (4)	0.3635 (4)	0.95041 (13)	0.0546 (7)
C3	0.7202 (5)	0.2284 (5)	0.98276 (13)	0.0588 (8)
C4	0.7738 (4)	0.0711 (4)	0.96915 (13)	0.0565 (8)
C5	0.8691 (5)	0.0501 (4)	0.92021 (14)	0.0548 (7)
C6	0.9125 (4)	0.1838 (4)	0.88756 (12)	0.0494 (7)
C7	0.7331 (7)	−0.0760 (6)	1.00576 (2)	0.0862 (13)
C8	0.8320 (3)	0.4630 (3)	0.79788 (11)	0.0420 (6)
C9	0.6446 (4)	0.4595 (4)	0.79664 (12)	0.0508 (7)
C10	0.5887 (4)	0.3595 (4)	0.74638 (14)	0.0522 (7)
C11	0.6811 (4)	0.4146 (4)	0.69368 (12)	0.0449 (6)
C12	0.9264 (3)	0.4328 (3)	0.75319 (11)	0.0407 (6)
C13	0.6377 (5)	0.3249 (4)	0.6392 (2)	0.0625 (8)
C14	0.6653 (6)	0.4585 (7)	0.5951 (2)	0.0785 (11)
C15	0.6204 (6)	0.6126 (5)	0.6258 (2)	0.0750 (11)
C16	1.11562 (4)	0.4248 (4)	0.74984 (15)	0.0585 (8)

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

S—O1	1.486 (3)	C8—C9	1.493 (4)
S—C8	1.773 (3)	C9—C10	1.511 (5)
S—C1	1.798 (3)	C10—C11	1.520 (4)
C1—C2	1.383 (5)	C11—O3	1.410 (4)
C1—C6	1.387 (4)	C11—O2	1.446 (4)
C2—C3	1.382 (5)	C11—C13	1.525 (5)
C3—C4	1.383 (5)	O2—C12	1.371 (3)
C4—C5	1.399 (5)	C12—C16	1.512 (4)
C4—C7	1.512 (5)	C13—C14	1.524 (6)
C5—C6	1.378 (4)	C14—C15	1.490 (6)
C8—C12	1.324 (4)	C15—O3	1.429 (4)
O1—S—C8	107.4 (2)	C8—C9—C10	108.7 (2)
O1—S—C1	105.7 (2)	C9—C10—C11	110.5 (2)
C8—S—C1	97.79 (12)	O3—C11—O2	108.3 (2)
C2—C1—C6	120.3 (3)	O3—C11—C10	108.7 (3)
C2—C1—S	119.8 (2)	O2—C11—C10	109.9 (2)
C6—C1—S	119.8 (2)	O3—C11—C13	106.6 (2)
C3—C2—C1	119.2 (3)	O2—C11—C13	106.3 (3)
C2—C3—C4	121.7 (3)	C10—C11—C13	116.7 (3)
C3—C4—C5	118.3 (3)	C12—O2—C11	118.1 (2)
C3—C4—C7	121.8 (3)	C8—C12—O2	122.7 (2)
C5—C4—C7	119.9 (3)	C8—C12—C16	128.1 (3)
C6—C5—C4	120.5 (3)	O2—C12—C16	109.2 (2)
C5—C6—C1	120.0 (3)	C14—C13—C11	102.2 (3)
C12—C8—C9	123.3 (3)	C15—C14—C13	103.0 (3)
C12—C8—S	119.7 (2)	O3—C15—C14	107.5 (3)
C9—C8—S	117.0 (2)	C11—O3—C15	110.1 (3)

The determination of the absolute configuration was possible from the known *S* configuration of the sulfoxide group in the starting heterodiene; using the method described by Flack (1983), the absolute configuration was confirmed by the calculations (*SHELXL*93; Sheldrick, 1993). H atoms were refined as rigid groups using the *AFIX* card of the *SHELXL*93 program.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990) option *TREF*. Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP* (Johnson, 1965).

The authors thank Professor M. Leblanc, University of Maine, for helpful discussions.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Diels–Alder Adduct of an Enantiopure 2-Sulfinyldiene and Maleimide: (1*S*,2*R*,3*S*,*SR*)-3-Methyl-5-*p*-toluenesulfinylcyclohex-4-en-1,2-dicarboximide

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Abstract

The title compound, $C_{16}H_{17}NO_3S$, is the single adduct obtained by cycloaddition of (*E*)-(+)-(*R*)-2-*p*-toluenesulfinyl-1,3-pentadiene with maleimide. The ab-

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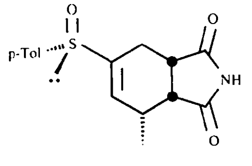
solute configuration of the stereocentres is established and some mechanistic aspects are deduced.

Comment

Control over asymmetric induction in Diels–Alder cycloadditions is a matter of continuing interest (Taschner, 1989). We reported recently that enantiopure 2-sulfinyldiene may readily be synthesized from (*SR*)-vinylsulfoxide (Bonfand, Gosselin & Maignan, 1993). We then examined the cycloaddition of (*E*)-(+)-(*R*)-2-*p*-toluenesulfinyl-1,3-pentadiene in order to study both *endo*/*exo* and diastereofacial selectivities. This diene was reacted with maleimide in ether at room temperature and the reaction was complete after 10 h. Only one of four possible stereoisomers, (I), was isolated.



(I)

The configuration of the three contiguous stereocentres was shown to be 1*S*,2*R*,3*S* (C12, C11 and C10, respectively) by single-crystal X-ray diffraction. The title compound results from an exclusive *endo* approach by a completely diastereofacial selective route, *i.e.* from the less hindered side of the diene, which is also the most nucleophilic. This indicates an *s-trans* conformation of the S=O and C=C bonds in the diene, at least in the transition state.

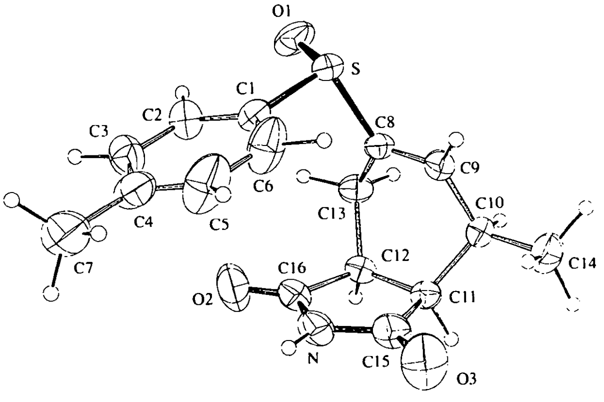


Fig. 1 *ORTEP* plot of $C_{16}H_{17}NO_3S$. For the sake of clarity the displacement parameters of the H atoms have been divided by ten. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Recrystallization from CH_2Cl_2/Et_2O afforded the title compound as colourless platelets and a parallelepipedic crystal was chosen for X-ray analysis. Its quality was tested using Laue photographs.

Crystal data

$C_{16}H_{17}NO_3S$
$M_r = 303.37$
Orthorhombic
$P2_12_12_1$
$a = 8.5143$ (7) Å
$b = 11.8171$ (6) Å
$c = 14.7520$ (9) Å
$V = 1484.3$ (2) Å^3
$Z = 4$
$D_x = 1.358$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 36 reflections
$\theta = 12.75$–$15.7°$
$\mu = 0.217$ mm^{-1}
$T = 293$ (2) K
Parallelepiped
0.608 × 0.532 × 0.456 mm
Colourless

Data collection

Stoe Siemens AED-2 diffractometer
ω–2θ scans
Absorption correction: none
4922 measured reflections
4328 independent reflections
3727 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0342$
$\theta_{max} = 30°$
$h = -11 \rightarrow 11$
$k = -16 \rightarrow 16$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity variation: 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0419$
$wR(F^2) = 0.1108$
$S = 0.994$
4318 reflections
227 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0908P)^2 + 0.0928P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.070$

$\Delta\rho_{max} = 0.248$ e Å^{-3}
$\Delta\rho_{min} = -0.219$ e Å^{-3}
Extinction correction: none
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)

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

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

	x	y	z	U_{eq}
S	0.14421 (5)	0.91874 (4)	0.81601 (3)	0.04102 (12)
N	0.3896 (2)	0.88709 (14)	0.53164 (10)	0.0444 (4)
O1	0.2347 (2)	0.97751 (14)	0.88926 (9)	0.0568 (4)
O2	0.5133 (3)	1.02400 (13)	0.61450 (13)	0.0700 (5)
O3	0.2948 (3)	0.7207 (2)	0.47557 (12)	0.0765 (6)
C1	0.1252 (2)	1.01846 (13)	0.72563 (10)	0.0356 (3)
C2	0.1936 (2)	1.1233 (2)	0.73248 (13)	0.0414 (4)
C3	0.1756 (2)	1.2012 (2)	0.6635 (2)	0.0493 (4)
C4	0.0905 (3)	1.1753 (2)	0.58651 (13)	0.0581 (6)
C5	0.0203 (5)	1.0698 (3)	0.5822 (2)	0.0845 (10)
C6	0.0356 (4)	0.9913 (2)	0.6512 (2)	0.0670 (7)
C7	0.0754 (5)	1.2613 (3)	0.5107 (2)	0.0887 (11)
C8	0.2774 (2)	0.82421 (13)	0.76250 (10)	0.0325 (3)
C9	0.2239 (2)	0.72916 (14)	0.72617 (12)	0.0374 (3)
C10	0.3391 (2)	0.65245 (12)	0.67886 (11)	0.0349 (3)
C11	0.4468 (2)	0.72360 (13)	0.61668 (10)	0.0308 (3)
C12	0.5161 (2)	0.82832 (14)	0.66435 (9)	0.0314 (3)
C13	0.4487 (2)	0.85171 (15)	0.75922 (11)	0.0363 (3)
C14	0.2588 (3)	0.5523 (2)	0.6320 (2)	0.0548 (5)
C15	0.3651 (2)	0.7725 (2)	0.53340 (11)	0.0422 (4)
C16	0.4769 (2)	0.9272 (2)	0.60267 (11)	0.0408 (3)

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

S—O1	1.498 (2)	C9—C10	1.507 (2)
S—C8	1.7766 (15)	C10—C14	1.532 (3)
S—C1	1.787 (2)	C10—C11	1.545 (2)
C1—C2	1.373 (2)	C11—C15	1.525 (2)
C1—C6	1.375 (3)	C11—C12	1.541 (2)
C2—C3	1.380 (3)	C12—C16	1.518 (2)
C3—C4	1.382 (3)	C12—C13	1.538 (2)
C4—C5	1.384 (5)	C15—O3	1.209 (2)
C4—C7	1.517 (3)	C15—N	1.370 (3)
C5—C6	1.383 (4)	C16—O2	1.197 (3)
C8—C9	1.325 (2)	C16—N	1.370 (2)
C8—C13	1.495 (2)		
O1—S—C8	106.49 (9)	C9—C10—C14	112.5 (2)
O1—S—C1	106.21 (8)	C9—C10—C11	109.49 (12)
C8—S—C1	98.10 (7)	C14—C10—C11	114.68 (15)
C2—C1—C6	120.3 (2)	C15—C11—C12	103.77 (13)
C2—C1—S	120.13 (13)	C15—C11—C10	114.44 (14)
C6—C1—S	119.5 (2)	C12—C11—C10	113.17 (11)
C1—C2—C3	120.0 (2)	C16—C12—C13	108.95 (14)
C4—C3—C2	121.1 (2)	C16—C12—C11	105.10 (12)
C3—C4—C5	117.7 (2)	C13—C12—C11	114.61 (12)
C3—C4—C7	120.1 (3)	C8—C13—C12	110.78 (13)
C5—C4—C7	122.2 (3)	O3—C15—N	124.2 (2)
C6—C5—C4	121.9 (2)	O3—C15—C11	127.0 (2)
C1—C6—C5	118.9 (2)	N—C15—C11	108.68 (15)
C9—C8—C13	120.42 (14)	O2—C16—N	125.6 (2)
C9—C8—S	119.56 (13)	O2—C16—C12	126.2 (2)
C13—C8—S	120.02 (12)	N—C16—C12	108.1 (2)
C8—C9—C10	118.26 (14)	C16—N—C15	114.23 (15)

The determination of the absolute configuration was possible from the known *R* configuration of the sulfoxide group in the starting diene; using the method described by Flack (1983), tha absolute configuration was confirmed by the calculations [*SHELXL*93 (Sheldrick, 1993) option applied on non-centrosymmetric space groups]. H atoms were refined as rigid groups using the *AFIX* card of the *SHELXS*93 program.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990), option *TREF*. Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-Ethyl-2′-deoxycytidine, $C_{11}H_{17}N_3O_4$

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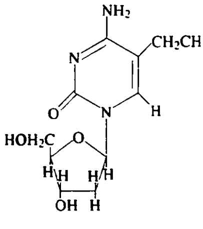
Abstract

The deoxyribose ring in the title compound adopts the twist conformation ($^{2}_{3}T$) with a glycosyl torsion angle of 231.0 (6)°. The pseudo-rotation parameters are P = 180.29 (5)° and τ_m = 38.3 (5)°. The exocyclic side chain at C5′ has the *t* conformation [γ = 174.8 (11)°]. The ethyl group at C5 is on the same side of the pyrimidine plane as the O4′ atom of the furanose ring.

Comment

5-Ethyl-2′-deoxyuridine (EtdUrd) has been shown to be a relatively potent inhibitor of herpes simplex virus (types 1 and 2) replication (De Clerq & Rosenwirth, 1985; De Clerq & Shugar, 1975; Schinazi, Scott, Peters, Rice & Nahmias, 1985). 5-Ethyl-2′-deoxycytidine (EtdCyd) was prepared as a potential antiviral agent, based on the potency of EtdUrd (De Clerq & Shugar, 1975; Kulikowski & Shugar, 1974).



EtdCyd

A perspective *ORTEP*II (Johnson, 1976) drawing of the molecule is shown in Fig. 1. The bond lengths and angles of EtdCyd are in the range reported for other 2′-deoxycytidine nucleosides (Young & Wilson, 1975; Kashino, Negishi & Hayatsu, 1988; Low, Tollin, Howie & Wilson, 1988; Sato, 1988; Silver-