C5—C6	1.499 (8)	C22—C23	1.496 (8)
C5—C10	1.514 (7)	C24—C25	1.592 (11)
C6—C7	1.536 (8)	C25—C26	1.459 (12)
C7—C8	1.530 (7)		
C24—O16—C16	119.3 (5)	C12—C13—C18	110.9 (4)
C22—O21—C21	116.4 (4)	C14—C13—C18	111.8 (4)
C2—C1—C10	124.1 (5)	C12—C13—C17	115.8 (4)
C1—C2—C3	121.5 (6)	C14—C13—C17	99.9 (3)
O3—C3—C4	122.5 (6)	C18—C13—C17	109.0 (4)
O3—C3—C2	120.5 (6)	C15—C14—C13	102.9 (4)
C4—C3—C2	117.0 (5)	C15—C14—C8	119.5 (4)
C5—C4—C3	123.0 (6)	C13—C14—C8	114.7 (4)
C4—C5—C6	122.8 (5)	C14—C15—C16	103.9 (4)
C4—C5—C10	122.2 (5)	O16—C16—C15	106.1 (4)
C6—C5—C10	114.9 (4)	O16—C16—C17	111.6 (4)
C5—C6—C7	111.8 (4)	C15—C16—C17	106.9 (4)
C8—C7—C6	113.7 (4)	O17—C17—C20	109.1 (4)
C7—C8—C9	110.6 (4)	O17—C17—C16	111.7 (4)
C7—C8—C14	109.8 (4)	C20—C17—C16	114.2 (4)
C9—C8—C14	108.3 (4)	O17—C17—C13	107.4 (4)
C11—C9—C8	115.4 (4)	C20—C17—C13	111.6 (4)
C11—C9—C10	114.9 (4)	C16—C17—C13	102.5 (4)
C8—C9—C10	111.5 (4)	O20—C20—C21	121.3 (5)
C1—C10—C5	112.1 (4)	O20—C20—C17	122.7 (5)
C1—C10—C19	106.5 (4)	C21—C20—C17	116.0 (4)
C5—C10—C19	108.0 (4)	O21—C21—C20	112.4 (5)
C1—C10—C9	110.4 (4)	O22—C22—O21	122.3 (5)
C5—C10—C9	106.3 (4)	O22—C22—C23	126.1 (5)
C19—C10—C9	113.5 (4)	O21—C22—C23	111.6 (5)
O11—C11—C12	113.0 (4)	O24—C24—O16	122.1 (6)
O11—C11—C9	109.2 (4)	O24—C24—C25	129.1 (6)
C12—C11—C9	112.5 (4)	O16—C24—C25	108.8 (6)
C13—C12—C11	113.4 (4)	C26—C25—C24	111.8 (8)
C12—C13—C14	109.0 (4)		

The structure of the title compound was solved by direct methods in the $P6_1$ and $P6_5$ space groups. Each of the *E* maps revealed all the non-H atoms of the steroid molecule and a low additional peak for the second molecule. Initial isotropic and anisotropic refinement cycles for only the steroid molecule gave a high final *R* value of 0.071, a peak of 1.17 e Å^{-3} near the 6_1 axis on the difference map, large e.s.d.'s for the positional parameters and significant differences between observed and calculated structure factors for a few reflections with small indices. All parameters were corrected after the setting of the peak by the O atom, with a site occupancy factor of 1, before isotropic refinement. As the presence of water molecules in the ratio 1:1 was confirmed by elemental analysis of the crystal, the water O atoms must be strongly disordered. The calculated percentage content of carbon is 65.8% for the unsolvated compound and 63.4% for the monohydrate compound, while the amount of carbon found was 63.6 (3)%. A similar problem with the hexagonal molecular arrangement has been discussed for the structure of avarol (Puliti, De Rosa & Mattia, 1994). The water H atoms could not be located from the difference maps. The alkyl H atoms at the C23, C25 and C26 atoms were fixed geometrically with riding models and $U = 1.2U_{eq}$(C). All other H atoms were located from the difference Fourier map and refined isotropically. The absolute structure was assigned to agree with the known configuration of the main steroid skeleton in the $P6_1$ space group. Parallel refinement of the unsuitable enantiomer in the $P6_5$ space group gave the same $R = 0.058$ and $wR = 0.1477$ values as for the $P6_1$ group.

Data collection: *Kuma KM-4 Software* (Kuma, 1991). Cell refinement: *Kuma KM-4 Software*. Data reduction: *Kuma KM-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: KA1173). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(R_S)-4-*p*-Toluenesulfinylcyclohexa-1,4-diene-carboxylic Acid Ethyl Ester

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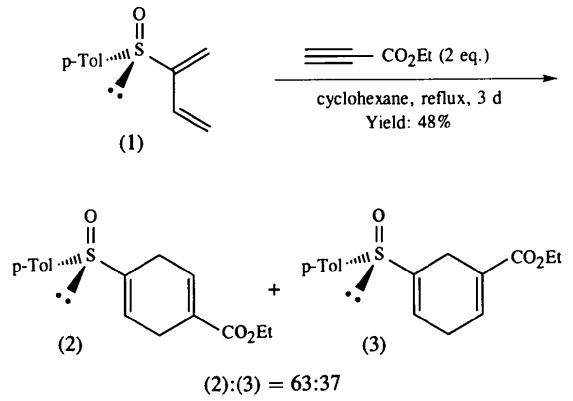
Abstract

The structure determination of $C_{16}H_{18}O_3S$ by single-crystal X-ray diffraction revealed the *para* regiochemistry of the title compound.

Comment

In connection with our interest in using chiral sulfoxides in asymmetric synthesis, we have studied both the reactivity and selectivity of enantiopure sulfinyl heterodiene

(Hayes & Maignan, 1994) and sulfinyl homodienes (Gosselin, Bonfand, Hayes, Retoux & Maignan, 1994) in asymmetric Diels–Alder reactions. In particular, we examined the cycloaddition of (+)-(*R*)-2-*p*-toluenesulfinyl-1,3-butadiene (1) with ethylpropiolate in order to study the regioselectivity.



Although spectroscopic analysis suggested the formation of the *para* (2) and *meta* (3) isomers, unambiguous confirmation of the structure was only possible by X-ray diffraction analysis. A perspective view of the structure of (R_S)-4-*p*-toluenesulfinylcyclohexa-1,4-dienecarboxylic acid ethyl ester reveals the *para* regiochemistry of the major adduct (Fig. 1).

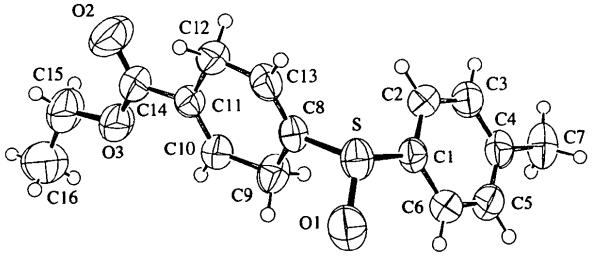


Fig. 1 *ORTEP* (Johnson, 1965) plot of $C_{16}H_{18}O_3S$. Displacement ellipsoids are plotted at the 50% probability level. H atoms are drawn as spheres of arbitrary radius.

Experimental

The diene (1) was reacted with the acetylenic dienophile in cyclohexane at 353 K for 3 d to give a 63:37 mixture of the two regioadducts which were easily separated by chromatography on silica gel. Recrystallization of the title compound from ether after liquid chromatography gave small colourless platelets. Suitable crystals for X-ray analysis were very difficult to find owing to the sharpness of the crystals. The quality of the chosen crystal was tested with Laue photographs.

Crystal data

$C_{16}H_{18}O_3S$
M_r = 290.37
Orthorhombic
$Pna2_1$
a = 27.668 (7) Å
b = 5.2391 (12) Å
c = 10.4134 (15) Å
V = 1509.5 (6) Å^3
Z = 4
D_x = 1.278 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 36 reflections
θ = 13.2–15.9°
μ = 0.219 mm^{-1}
T = 293 (2) K
Plate
0.646 × 0.380 × 0.114 mm
Colourless

Data collection

Stoe Siemens AED-2 diffractometer
ω scans
Absorption correction: none
3655 measured reflections
3463 independent reflections
2250 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0394
θ_{max} = 27.51°
$h = -35 \rightarrow 35$
$k = -6 \rightarrow 6$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: 7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0420
$wR(F^2)$ = 0.1315
S = 0.984
3456 reflections
215 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0813P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.171 e Å^{-3}
$\Delta\rho_{min}$ = −0.150 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)
Flack parameter = 0.33 (11)

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	0.28431 (2)	0.26880 (12)	0.96320 (8)	0.0633 (2)
O1	0.28815 (9)	0.2837 (5)	1.1058 (2)	0.0853 (7)
O2	0.06014 (10)	−0.1036 (6)	0.7870 (3)	0.1123 (9)
O3	0.07276 (7)	−0.3650 (5)	0.9508 (2)	0.0827 (6)
C1	0.32399 (9)	0.0155 (5)	0.9133 (2)	0.0539 (6)
C2	0.32287 (9)	−0.0759 (5)	0.7887 (3)	0.0602 (6)
C3	0.35604 (11)	−0.2599 (5)	0.7518 (3)	0.0643 (7)
C4	0.38965 (9)	−0.3579 (6)	0.8366 (3)	0.0619 (7)
C5	0.38963 (9)	−0.2653 (6)	0.9601 (4)	0.0710 (7)
C6	0.35762 (9)	−0.0774 (6)	0.9994 (2)	0.0640 (7)
C7	0.42421 (11)	−0.5645 (6)	0.7944 (4)	0.0839 (10)
C8	0.22816 (9)	0.1189 (5)	0.9281 (2)	0.0537 (6)
C9	0.21515 (9)	−0.1121 (5)	1.0050 (3)	0.0637 (7)
C10	0.16485 (8)	−0.1987 (5)	0.9782 (3)	0.0581 (6)
C11	0.13615 (10)	−0.0938 (5)	0.8905 (2)	0.0545 (6)
C12	0.15168 (10)	0.1209 (5)	0.8054 (3)	0.0617 (6)
C13	0.19974 (10)	0.2271 (5)	0.8416 (3)	0.0584 (6)
C14	0.08608 (11)	−0.1861 (6)	0.8693 (3)	0.0665 (8)
C15	0.02425 (13)	−0.4679 (9)	0.9410 (4)	0.1021 (13)
C16	0.0128 (2)	−0.5964 (14)	1.0567 (5)	0.153 (3)

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

S—O1	1.490 (3)	C8—C9	1.496 (4)
S—C8	1.779 (3)	C9—C10	1.490 (3)
S—C1	1.799 (3)	C10—C11	1.329 (4)
C1—C6	1.380 (4)	C11—C14	1.484 (4)

C1—C2	1.384 (4)	C11—C12	1.495 (4)
C2—C3	1.385 (4)	C12—C13	1.490 (4)
C3—C4	1.381 (4)	C14—O2	1.199 (4)
C4—C5	1.375 (5)	C14—O3	1.317 (4)
C4—C7	1.510 (4)	O3—C15	1.450 (4)
C5—C6	1.386 (4)	C15—C16	1.416 (6)
C8—C13	1.323 (4)		
O1—S—C8	106.89 (13)	C13—C8—S	118.0 (2)
O1—S—C1	106.42 (14)	C9—C8—S	117.2 (2)
C8—S—C1	98.50 (11)	C10—C9—C8	111.7 (2)
C6—C1—C2	120.1 (2)	C11—C10—C9	124.1 (3)
C6—C1—S	118.9 (2)	C10—C11—C14	121.7 (3)
C2—C1—S	120.8 (2)	C10—C11—C12	123.1 (2)
C1—C2—C3	119.1 (3)	C14—C11—C12	115.2 (2)
C4—C3—C2	121.9 (3)	C13—C12—C11	112.8 (2)
C5—C4—C3	117.8 (3)	C8—C13—C12	122.9 (3)
C5—C4—C7	121.7 (3)	O2—C14—O3	123.3 (3)
C3—C4—C7	120.5 (3)	O2—C14—C11	123.2 (3)
C4—C5—C6	121.8 (3)	O3—C14—C11	113.4 (3)
C1—C6—C5	119.3 (3)	C14—O3—C15	118.6 (3)
C13—C8—C9	124.6 (2)	C16—C15—O3	109.0 (3)

The absolute configuration was assigned to agree with the known chirality of the sulfoxide group as established by the synthesis of (1) (Bonfand, Gosselin & Maignan, 1992) and the method described by Flack (1983) was used to confirm the absolute configuration $\chi = 0.33\,(11)$ [compared to $\chi = 0.67\,(11)$ for the inverted absolute structure (*SHELXL*93 option applied on non-centrosymmetric space groups)]. H atoms were refined as rigid groups with their neighbours using *AFIX* in *SHELXL*93 (Sheldrick, 1993).

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: *PATT SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1227). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Conformationally Restricted Aspartic Acid Analogue with a Bicyclo-[2.2.2]octane Skeleton

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Abstract

The bicyclo[2.2.2]octane cage in (2*R*,3*S*)-3-benzamido-3-methoxycarbonylbicyclo[2.2.2]octane-2-carboxylic acid, $C_{18}H_{21}NO_5$, has approximate D_3 symmetry and the three six-membered rings of this fragment all deviate slightly from ideal boat conformations. The values determined for the torsion angles about the N—Cα (φ) and Cα—CO (ψ) bonds correspond to a semi-extended conformation for the amino acid residue. The crystal structure is stabilized by two intermolecular hydrogen bonds (O—H···O and N—H···O) involving the carboxylic acid, the benzamido and the methyl ester groups.

Comment

Whereas the synthesis of amino acids has been a matter of longstanding interest (Duthaler, 1994; Williams, 1989), the synthesis of conformationally constrained amino acids has only attracted significant attention in the past decade when it has been recognized that their incorporation into peptides is a powerful approach for generating structurally defined peptides as conformational probes and bioactive agents (Liskamp, 1994; Gante, 1994). In this context, and as part of our research project on the stereoselective synthesis of new non-proteinogenic and unusual conformationally restricted amino acids, we have developed a new methodology involving the use of *Z*-2-phenyl-4-[(*S*)-2,2-dimethyl-1,3-dioxolan-4-ylmethylen]-5(4*H*)-oxazolone as dienophile in Diels–Alder reactions with different dienes allowing the synthesis of new and interesting compounds (Buñuel, Cativiela & Díaz-de-Villegas, 1994, 1995; Buñuel, Cativiela, Díaz-de-Villegas & Garcia, 1994.

In a previous paper, we reported the crystal structure of an aspartic acid analogue with a norbornyl skeleton (Buñuel, Cativiela, Díaz-de-Villegas & Gálvez, 1996), and now we describe here the crystal and molecular structure of another conformationally restricted aspartic acid analogue (I) with a bicyclo[2.2.2]octane skeleton.