Benhamou, B., Garcia, T., Lerouge, T., Vergezac, A., Gofflo, D., Bigogne, C., Chambon, P. & Gronemeyer, H. (1992). *Science*, **255**, 206–209.
Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure*, Vol. I. New York: Plenum.
Geerestein, V. J. van, Kanters, J. A. & Kroon, J. (1987). *Acta Cryst.* C**43**, 319–322.
Geerestein, V. J. van, Kanters, J. A., van der Sluis, P. & Kroon, J. (1986). *Acta Cryst.* C**42**, 1521–1523.
Griffin, J. F., Duax, W. L. & Weeks, C. M. (1984). *Atlas of Steroid Structure*, Vol. II. New York: Plenum.
Heikinheimo, O., Ylikorkala, O. & Lahteenmaki, P. (1990). *Ann. Med. (Hagerstown, Md)*. **22**, 75–84.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Palmer, R. A., Palmer, H. T., Lisgarten, J. N. & Lancaster, R. (1993). *Acta Cryst.* C**49**, 721–723.
Roszak, A. W. & Codding, P. W. (1990). *Acta Cryst.* C**46**, 1700–1704.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Release 4.11/V. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.
Ulmann, A. & Dubois, C. (1989). *Acta Obstet. Gynecol. Scand. Suppl.* **149**, 9–11.

Acta Cryst. (1994). C**50**, 2093–2094

(3*S*,3a*R*,4*R*,7*S*,7a*S*,*SS*)-3-Ethoxy-3a,4,7,7a-tetrahydro-4,7-methano-7a-*p*-tolysulfinyl-1(3*H*)-isobenzofuranone

M. SORIANO-GARCIA,* A. RODRÍGUEZ-ROMERO, R. VILLENA AND F. YUSTE

Instituto de Química,† Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, México DF

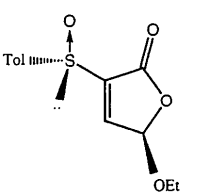
(*Received* 5 *April* 1994; *accepted* 3 *May* 1994)

Abstract

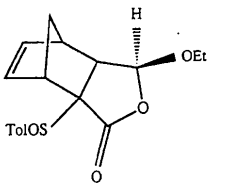
The molecular structure of the title compound, $C_{18}H_{20}O_4S$, determined from the X-ray data confirms the structure previously assigned on the basis of chemical and spectroscopic evidence. The S atom has the usual distorted tetrahedral configuration. The molecular skeleton of the molecule comprises a system of three five-membered rings (*A*, *B* and *C*). The *A* and *B* rings are *cis* fused; all three five-membered rings adopt envelope conformations. The crystal structure is stabilized entirely by van der Waals forces and three C—H···O hydrogen-bond interactions.

Comment

The thermal and catalysed Diels–Alder reactions of (5*S*,*SS*)-5-ethoxy-3-*p*-tolysulfinyl-2(5*H*)-furanone (1) with cyclopentadiene in dichloromethane afford the adduct (2) as the principal product.



(1)



(2)

The empirical formula of (2), $C_{18}H_{20}O_4S$, was established by high-resolution mass spectrometry and the functional groups present in the molecule were characterized by IR and NMR spectroscopy (Carretero, García, Ruano, Lorente & Yuste, 1993).

The *A* and *B* rings are *cis* fused at the C(3*A*)—C(7*A*) bond and the *B* and *C* rings are fused at C(4)—C(8)—C(7). The *A*, *B* and *C* five-membered rings are in envelope conformations. The Δ and ϕ values (Altona, Geise & Romers, 1968) of these rings, *A*, *B* and *C*, are 32.2 (4) and 4.7 (4)°, 40.3 (4) and 62.6 (4)° and 33.3 (5) and 52.1 (5)°, respectively. The packing in the crystal is entirely due to van der Waals forces and three C—H···O hydrogen-bond interactions of < 3.5 Å: C(4)···O(1) 3.410 (6), C(5)···O(4)(1−*x*, −0.5 + *y*, 1.5−*z*) 3.487 (6) and C(13)···O(4)(−*x*, −0.5 + *y*, 1.5−*z*) 3.338 (5) Å.

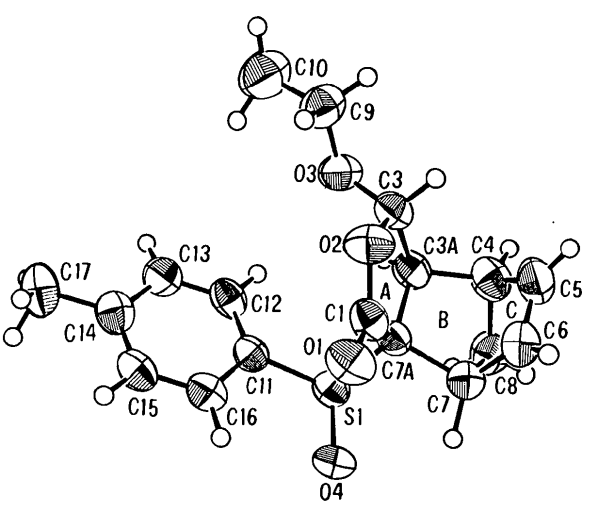


Fig. 1. The molecular structure of the title compound with numbering. The displacement ellipsoids are drawn at the 50% probability level.

Experimental

A solution of (1) (0.2 mmol, 1 eq.) in CH_2Cl_2 (2.5 ml) was added to a cooled (273 K) stirred solution of $ZnBr_2$ (0.24 mmol, 1.2 eq.) in 2.5 ml of CH_2Cl_2. After stirring for 15 min, cyclopentadiene (1.2 mmol, 6 eq.) was added and the mixture was stirred for a further hour. Aqueous $NaHCO_3$ (10%, 10 ml) was added to the mixture. The organic phase

† Contribution No. 1236 of the Instituto de Química, UNAM.

was separated and the aqueous layer extracted with CH_2Cl_2 (2 × 15 ml). The combined organic extracts were dried (Na_2SO_4) and evaporated. The mixture of adducts was studied by ^1H NMR and separated by flash chromatography using 95:5 dichloromethane–ethyl ether as eluent; (2) was produced in 70% yield. Crystals were obtained from acetone–hexane solution.

Crystal data

$C_{18}H_{20}O_4S$	Cu $K\alpha$ radiation
M_r = 332.41	λ = 1.5418 Å
Orthorhombic	Cell parameters from 25 reflections
$P2_12_12_1$	θ = 12–38°
a = 9.829 (3) Å	μ = 1.842 mm^{-1}
b = 11.632 (4) Å	T = 293 K
c = 14.482 (3) Å	Prism
V = 1656 (1) Å^3	0.40 × 0.22 × 0.20 mm
Z = 4	Colourless
D_x = 1.33 Mg m^{-3}	

Data collection

Nicolet *P3/F* diffractometer	θ_{max} = 55°
$2\theta/\theta$ scans	$h = 0 \rightarrow 10$
Absorption correction: none	$k = 0 \rightarrow 12$
1296 measured reflections	$l = 0 \rightarrow 15$
1244 independent reflections	2 standard reflections monitored every 50 reflections
1168 observed reflections [$I > 3.0\sigma(I)$]	intensity variation: 3%

Refinement

Refinement on F	$\Delta\rho_{max}$ = 0.18 e Å^{-3}
R = 0.039	$\Delta\rho_{min}$ = −0.16 e Å^{-3}
wR = 0.058	Extinction correction: Zachariasen (1968)
S = 2.49	Extinction coefficient: 5.5 (10) × 10^{-6}
1168 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
209 parameters	
Only coordinates of H atoms refined	
$w = 1/[\sigma^2(F_o) + 0.0031(F_o)^2]$	
$(\Delta/\sigma)_{max}$ = 0.054	

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

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
S(1)	0.1612 (1)	0.11332 (8)	0.80347 (6)	4.26 (5)
O(1)	0.3592 (3)	0.1569 (3)	0.6214 (2)	5.2 (1)
O(2)	0.3478 (3)	−0.0342 (2)	0.6103 (2)	5.0 (1)
O(3)	0.2117 (3)	−0.1906 (2)	0.6410 (2)	5.1 (1)
O(4)	0.1975 (3)	0.2365 (2)	0.8150 (2)	5.5 (1)
C(1)	0.3418 (4)	0.0659 (4)	0.6579 (3)	4.2 (2)
C(3)	0.3264 (4)	−0.1355 (3)	0.6681 (3)	4.4 (2)
C(3A)	0.3117 (4)	−0.0894 (3)	0.7666 (3)	4.3 (2)
C(4)	0.4332 (5)	−0.1149 (5)	0.8338 (3)	5.7 (2)
C(5)	0.5621 (5)	−0.0822 (5)	0.7857 (4)	5.8 (2)
C(6)	0.5634 (5)	0.0325 (5)	0.7794 (4)	5.6 (2)
C(7)	0.4354 (4)	0.0764 (4)	0.8253 (3)	4.9 (2)
C(7A)	0.3146 (4)	0.0406 (3)	0.7582 (3)	3.8 (2)
C(8)	0.4152 (6)	−0.0145 (5)	0.9004 (3)	5.8 (2)
C(9)	0.2239 (5)	−0.2486 (5)	0.5533 (4)	5.8 (2)
C(10)	0.0937 (7)	−0.2977 (8)	0.5291 (5)	7.6 (3)
C(11)	0.0460 (4)	0.1051 (3)	0.7081 (3)	4.0 (2)
C(12)	−0.0344 (5)	0.0100 (4)	0.6959 (3)	4.8 (2)
C(13)	−0.1371 (5)	0.0106 (4)	0.6304 (3)	4.9 (2)
C(14)	−0.1616 (4)	0.1083 (4)	0.5780 (3)	4.6 (2)
C(15)	−0.0780 (5)	0.2032 (4)	0.5904 (3)	4.8 (2)
C(16)	0.0252 (5)	0.2025 (4)	0.6561 (3)	4.5 (2)
C(17)	−0.2750 (6)	0.1109 (6)	0.5083 (4)	6.4 (3)

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

S(1)—O(4)	1.486 (3)	C(4)—C(8)	1.526 (7)
S(1)—C(7A)	1.849 (4)	C(5)—C(6)	1.337 (7)
S(1)—C(11)	1.788 (4)	C(6)—C(7)	1.512 (7)
O(1)—C(1)	1.196 (5)	C(7)—C(7A)	1.589 (6)
O(2)—C(1)	1.354 (5)	C(7)—C(8)	1.529 (7)
O(2)—C(3)	1.461 (5)	C(9)—C(10)	1.445 (9)
O(3)—C(3)	1.355 (5)	C(11)—C(12)	1.371 (6)
O(3)—C(9)	1.442 (6)	C(11)—C(16)	1.377 (5)
C(1)—C(7A)	1.506 (6)	C(12)—C(13)	1.385 (7)
C(3)—C(3A)	1.531 (6)	C(13)—C(14)	1.388 (6)
C(3A)—C(4)	1.570 (6)	C(14)—C(15)	1.388 (6)
C(3A)—C(7A)	1.517 (6)	C(14)—C(17)	1.504 (7)
C(4)—C(5)	1.494 (8)	C(15)—C(16)	1.390 (7)
O(4)—S(1)—C(7A)	106.5 (2)	C(6)—C(7)—C(8)	100.8 (4)
O(4)—S(1)—C(11)	106.9 (2)	C(7A)—C(7)—C(8)	99.1 (3)
C(7A)—S(1)—C(11)	102.6 (2)	S(1)—C(7A)—C(1)	113.4 (3)
C(1)—O(2)—C(3)	113.3 (3)	S(1)—C(7A)—C(3A)	114.3 (3)
C(3)—O(3)—C(9)	114.0 (3)	S(1)—C(7A)—C(7)	105.8 (3)
O(1)—C(1)—O(2)	122.0 (4)	C(1)—C(7A)—C(3A)	105.9 (3)
O(1)—C(1)—C(7A)	128.6 (4)	C(1)—C(7A)—C(7)	114.0 (3)
O(2)—C(1)—C(7A)	109.4 (3)	C(3A)—C(7A)—C(7)	103.1 (3)
O(2)—C(3)—O(3)	109.6 (4)	C(4)—C(8)—C(7)	93.7 (4)
O(2)—C(3)—C(3A)	105.4 (3)	O(3)—C(9)—C(10)	109.0 (4)
O(3)—C(3)—C(3A)	110.9 (3)	S(1)—C(11)—C(12)	120.5 (3)
C(3)—C(3A)—C(4)	116.0 (3)	S(1)—C(11)—C(16)	118.2 (3)
C(3)—C(3A)—C(7A)	105.8 (3)	C(12)—C(11)—C(16)	120.5 (4)
C(4)—C(3A)—C(7A)	102.9 (4)	C(11)—C(12)—C(13)	120.3 (4)
C(3A)—C(4)—C(5)	108.0 (4)	C(12)—C(13)—C(14)	120.4 (4)
C(3A)—C(4)—C(8)	99.1 (4)	C(13)—C(14)—C(15)	118.5 (4)
C(5)—C(4)—C(8)	101.4 (4)	C(13)—C(14)—C(17)	120.8 (4)
C(4)—C(5)—C(6)	107.1 (5)	C(15)—C(14)—C(17)	120.7 (4)
C(5)—C(6)—C(7)	107.4 (5)	C(14)—C(15)—C(16)	121.1 (4)
C(6)—C(7)—C(7A)	105.3 (4)	C(11)—C(16)—C(15)	119.2 (4)

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (*TEXSAN*; Molecular Structure Corporation, 1990). Least-squares refinement included of all non-H atoms, treated anisotropically. The H-atom positions in the CH, CH_2 and CH_3 groups were generated. Their positions were refined and included in the structure-factor calculations.

We are greatly indebted to Mrs Cynthia E. Lesh for her technical assistance. This work was supported by the Consejo Nacional de Cienca y Tecnologia de Mexico CONACYT, project No. 1304–E9205.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.

Carretero, J. C., García Ruano, J. L., Lorente, A. & Yuste, F. (1993). *Tetrahedron Asymmetry*, **4**, 177–180.

Molecular Structure Corporation (1990). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.