(II)				
O1	0.0	0.3236 (4)	0.0	0.057 (1)
O2	−0.0291 (3)	−0.1345 (3)	−0.1591 (3)	0.0495 (9)
C1	0.1310 (3)	0.3687 (5)	−0.1725 (4)	0.039 (1)
C2	0.0001 (4)	0.3511 (5)	−0.1218 (4)	0.041 (1)
C3	−0.1278 (4)	0.3772 (5)	−0.2236 (5)	0.047 (1)
C4	−0.1458 (3)	0.2753 (5)	−0.3660 (4)	0.038 (1)
C5	−0.2869 (4)	0.3058 (6)	−0.4500 (5)	0.056 (2)
C6	−0.3679 (4)	0.1313 (7)	−0.4138 (6)	0.071 (2)
C7	−0.2722 (4)	−0.0212 (6)	−0.3339 (5)	0.057 (2)
C8	−0.1368 (3)	0.0458 (6)	−0.3587 (4)	0.039 (1)
C9	−0.0194 (4)	−0.0322 (5)	−0.2585 (4)	0.037 (1)
C10	0.1148 (4)	0.0229 (6)	−0.2870 (4)	0.041 (1)
C11	0.1948 (4)	0.1613 (5)	−0.1784 (4)	0.041 (1)
C12	0.3347 (4)	0.1825 (7)	−0.2100 (5)	0.059 (2)
C13	0.4218 (4)	0.3234 (8)	−0.1084 (6)	0.074 (2)
C14	0.3574 (4)	0.5262 (8)	−0.1114 (6)	0.074 (2)
C15	0.2219 (4)	0.5085 (7)	−0.0728 (5)	0.055 (1)
(III)				
O1	0.2207 (1)	0.2154 (2)	0.5766 (3)	0.0573 (9)
O2	0.2060 (1)	0.3693 (2)	0.1413 (3)	0.0591 (9)
C1	0.3138 (1)	0.3819 (3)	0.6057 (4)	0.036 (1)
C2	0.2368 (2)	0.3373 (3)	0.6067 (4)	0.041 (1)
C3	0.1811 (2)	0.4426 (3)	0.6554 (4)	0.042 (1)
C4	0.1315 (2)	0.4918 (3)	0.4884 (4)	0.044 (1)
C5	0.0791 (2)	0.3830 (3)	0.3972 (4)	0.051 (1)
C6	0.0472 (2)	0.4524 (4)	0.2165 (5)	0.058 (1)
C7	0.0986 (2)	0.5721 (4)	0.1764 (5)	0.059 (1)
C8	0.1654 (2)	0.5574 (3)	0.3190 (4)	0.041 (1)
C9	0.2227 (2)	0.4674 (3)	0.2451 (4)	0.042 (1)
C10	0.2999 (2)	0.5023 (3)	0.2933 (4)	0.044 (1)
C11	0.3236 (1)	0.5196 (3)	0.5015 (4)	0.035 (1)
C12	0.4026 (2)	0.5636 (4)	0.5222 (4)	0.052 (1)
C13	0.4321 (2)	0.5739 (4)	0.7260 (5)	0.059 (1)
C14	0.4244 (2)	0.4349 (4)	0.8249 (5)	0.066 (2)
C15	0.3449 (2)	0.3909 (3)	0.8106 (4)	0.051 (1)
(IV)				
O1	0.7735 (2)	0.2650 (3)	0.4737 (2)	0.057 (1)
O2	0.4300 (2)	0.1575 (3)	0.4187 (2)	0.055 (1)
C1	0.6685 (3)	0.1701 (4)	0.5637 (3)	0.046 (2)
C2	0.7204 (3)	0.1797 (5)	0.4874 (2)	0.044 (2)
C3	0.7046 (3)	0.0783 (4)	0.4288 (3)	0.049 (2)
C4	0.7876 (3)	0.0573 (5)	0.3761 (3)	0.088 (3)
C5	0.7470 (4)	−0.0074 (6)	0.3061 (3)	0.087 (3)
C6	0.6601 (4)	0.0572 (6)	0.2926 (3)	0.120 (4)
C7	0.6189 (3)	0.0962 (5)	0.3727 (3)	0.055 (2)
C8	0.5750 (3)	0.2208 (5)	0.3653 (2)	0.054 (2)
C9	0.4951 (3)	0.2573 (4)	0.4202 (3)	0.047 (2)
C10	0.5250 (3)	0.2834 (4)	0.5050 (3)	0.045 (2)
C11	0.5594 (3)	0.1749 (4)	0.5548 (2)	0.042 (2)
C12	0.5311 (3)	0.1903 (5)	0.6411 (3)	0.063 (2)
C13	0.6022 (4)	0.2794 (5)	0.6753 (3)	0.065 (2)
C14	0.6902 (3)	0.2696 (5)	0.6247 (3)	0.066 (2)
C15	0.4495 (4)	0.3719 (5)	0.3877 (3)	0.071 (3)

Table 2. *Selected bond lengths* (Å) *and torsion angles* (°)

	(I)	(II)	(III)	(IV)
C1—C11	1.539 (4)	1.545 (5)	1.543 (4)	1.566 (6)
C4—C8	1.555 (4)	1.543 (5)	1.560 (4)	
C3—C7				1.567 (7)
C2—C1—C11—C10	−57.1 (3)	65.6 (4)	−65.1 (3)	−50.4 (5)
C3—C4—C8—C9	54.4 (4)	−48.7 (4)	52.6 (4)	
C2—C3—C7—C8				15.8 (6)

The calculations were carried out either on a FACOM M-780/10 computer using the *UNICS*III (Sakurai & Kobayashi, 1979) program system or on a MIPS 3230 workstation with the *Xtal*3.0 (Hall & Stewart, 1990) program system.

In (II), the systematic absences *h0l*, *l* odd suggested that the space group is *Pc* or *P2/c*. Since *Z* = 2 and the molecule does not have a centre of inversion or a twofold axis, the space group was determined to be *Pc*.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71252 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1027]

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Structure of a Bis-spiroacetal, *cis*-14-Phenylsulfonyl-1,7,9-trioxadispiro[5.1.5.3]-hexadecane

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Abstract

The crystal structure of the title compound has been determined by X-ray crystallography. The two terminal rings have chair conformations, while the central ring is disordered between distorted boat and chair structures.

The three O atoms have a *cis* configuration, confirming the similarity of this compound to certain antibiotic ionophores.

Comment

The bis-spiroacetal was prepared (Brimble, Rush, Williams & Baker, 1990) during an investigation of synthetic pathways to polyether antibiotics, such as salinomycin (Kinashi, Otake, Yonehara, Sato & Saito, 1973) and narasin (Occolowitz, Berg, Debono & Hamill, 1976). Two isomers were obtained; one was established as the *trans* isomer by X-ray crystallography, while the other was deduced as the *cis* isomer from ^{1}H and ^{13}C NMR spectra (Brimble, Rush, Williams & Baker, 1990). In order to confirm the stereochemistry of the latter isomer, and because of the potential of bis-spiroacetals to act as ionophores, a crystal structure analysis has been carried out.

The crystal structure confirmed the configuration proposed on the basis of the NMR data. The O atoms of the two terminal rings are *cis* to each other, occupying axial positions on the central ring which allow maximum stabilization by the anomeric effect. The two terminal rings have chair conformations, but the central ring is flexible, showing twofold disorder between a boat conformation (the major conformer, with an occupancy of 0.65) and a chair conformation (the minor conformer, with an occupancy of 0.35). This disorder limited the precision of the X-ray analysis. The O-atom positions are not affected by this disorder, however, and remain among the best-defined atoms in the molecule.

The cavity created by this particular array of C—O bonds makes this compound an interesting model for examining the ionophoric capability of bis-spiroacetals. The naturally occurring polyether antibiotics salinomycin (Kinashi, Otake, Yonehara, Sato & Saito, 1973) and narasin (Occolowitz, Berg, Debono & Hamill, 1976) bear some resemblance to the title compound in that they contain a similar *cis* bis-spiroacetal unit.

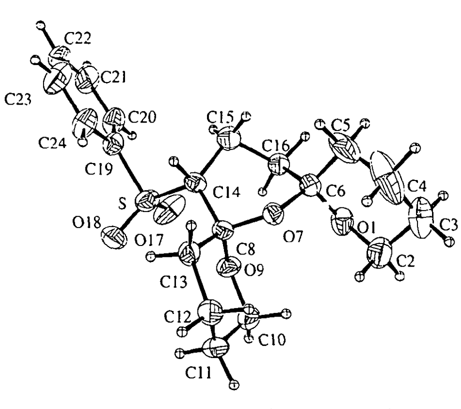

Fig. 1. The molecular structure of the title compound. Atoms are represented as 30% thermal ellipsoids. Only the major conformation at C15, C16 is shown.

Experimental

Crystal data

$C_{19}H_{26}O_5S$
M_r = 366.47
Monoclinic
$P2_1/n$
a = 5.856 (5) Å
b = 21.758 (4) Å
c = 14.495 (4) Å
β = 98.16 (5)°
V = 1828.2 (17) Å^3
Z = 4
D_x = 1.331 Mg m^{-3}
D_m (flotation) = 1.31 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.70930 Å
Cell parameters from 25 reflections
θ = 12.00–15.00°
μ = 0.19 mm^{-1}
T = 293 K
Needle
0.50 × 0.10 × 0.08 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2222 measured reflections
1708 independent reflections
1156 observed reflections [$I_{\rm net} > 2.0\sigma(I_{\rm net})$]

$R_{\rm int}$ = 0.014
$\theta_{\rm max}$ = 19.94°
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity variation: 5.0%

Refinement

Refinement on F
Final R = 0.051
wR = 0.061
S = 1.35
1156 reflections
224 parameters
H atoms not refined
$w = 1/[\sigma^2(F)+0.0010F^2]$
$(\Delta/\sigma)_{\rm max}$ = 0.007

$\Delta\rho_{\rm max}$ = 0.18 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.19 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	$U_{\rm eq}$
S	0.5685 (3)	0.15111 (8)	0.64487 (14)	0.068 (1)
O1	0.7249 (6)	−0.07976 (18)	0.7233 (3)	0.068 (3)
O7	0.9458 (6)	0.00840 (16)	0.7615 (3)	0.050 (2)
O9	0.5896 (6)	0.05360 (18)	0.7789 (3)	0.059 (2)
O17	0.3498 (7)	0.12266 (24)	0.6116 (4)	0.105 (4)
O18	0.5840 (10)	0.19131 (22)	0.7229 (3)	0.095 (4)
C2	0.8149 (14)	−0.1153 (3)	0.8021 (6)	0.089 (5)
C3	1.0175 (14)	−0.1527 (3)	0.7852 (7)	0.109 (6)
C4	1.1955 (13)	−0.1076 (4)	0.7572 (10)	0.153 (9)
C5	1.0937 (14)	−0.0699 (4)	0.6768 (8)	0.128 (8)
C6	0.8791 (11)	−0.0378 (3)	0.6915 (5)	0.064 (4)
C8	0.8165 (9)	0.0639 (3)	0.7614 (4)	0.047 (3)
C10	0.5700 (11)	0.0316 (3)	0.8700 (5)	0.074 (5)
C11	0.6866 (14)	0.0737 (3)	0.9441 (5)	0.090 (5)
C12	0.9378 (14)	0.0827 (3)	0.9320 (5)	0.079 (5)
C13	0.9530 (11)	0.1045 (3)	0.8336 (4)	0.057 (4)
C14	0.7929 (9)	0.0945 (3)	0.6646 (4)	0.050 (4)
C15	0.8013 (16)	0.0525 (4)	0.5801 (7)	0.065 (3)
C15*A*	0.694 (3)	0.0417 (7)	0.5944 (12)	0.051 (5)
C16	0.7021 (15)	−0.0093 (4)	0.6059 (7)	0.054 (3)
C16*A*	0.863 (3)	−0.0111 (8)	0.6018 (14)	0.067 (5)
C19	0.6503 (10)	0.1932 (3)	0.5507 (5)	0.059 (4)
C20	0.5161 (12)	0.1943 (3)	0.4665 (5)	0.076 (5)

C21	0.5826 (15)	0.2291 (3)	0.3948 (5)	0.098 (6)
C22	0.7849 (14)	0.2608 (3)	0.4079 (6)	0.097 (6)
C23	0.9193 (13)	0.2591 (4)	0.4922 (7)	0.106 (6)
C24	0.8519 (12)	0.2258 (3)	0.5645 (5)	0.084 (5)

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

S—O17	1.442 (5)	C8—C13	1.509 (8)
S—O18	1.422 (5)	C8—C14	1.541 (8)
S—C14	1.795 (6)	C10—C11	1.501 (11)
S—C19	1.766 (7)	C11—C12	1.519 (11)
O1—C2	1.418 (9)	C12—C13	1.518 (9)
O1—C6	1.407 (7)	C14—C15	1.534 (12)
O7—C6	1.442 (7)	C14—C15*A*	1.587 (17)
O7—C8	1.425 (7)	C15—C16	1.530 (13)
O9—C8	1.406 (6)	C15*A*—C16*A*	1.507 (24)
O9—C10	1.424 (8)	C19—C20	1.354 (10)
C2—C3	1.487 (11)	C19—C24	1.368 (9)
C3—C4	1.527 (13)	C20—C21	1.385 (10)
C4—C5	1.480 (17)	C21—C22	1.361 (12)
C5—C6	1.480 (10)	C22—C23	1.357 (13)
C6—C16	1.623 (11)	C23—C24	1.376 (11)
C6—C16*A*	1.416 (21)		
O17—S—O18	118.9 (4)	O9—C8—C13	112.9 (5)
O17—S—C14	110.7 (3)	O9—C8—C14	105.6 (4)
O17—S—C19	106.8 (3)	C13—C8—C14	110.4 (5)
O18—S—C14	109.5 (3)	O9—C10—C11	111.7 (5)
O18—S—C19	107.6 (3)	C10—C11—C12	110.3 (5)
C14—S—C19	101.9 (3)	C11—C12—C13	109.6 (6)
C2—O1—C6	115.8 (5)	C8—C13—C12	111.9 (5)
C6—O7—C8	119.9 (4)	S—C14—C8	114.2 (4)
C8—O9—C10	115.1 (4)	S—C14—C15	112.8 (5)
O1—C2—C3	112.3 (7)	S—C14—C15*A*	101.8 (6)
C2—C3—C4	106.5 (6)	C8—C14—C15	117.4 (6)
C3—C4—C5	110.6 (7)	C8—C14—C15*A*	104.4 (7)
C4—C5—C6	113.8 (8)	C14—C15—C16	105.8 (7)
O1—C6—O7	110.2 (5)	C14—C15*A*—C16*A*	109.3 (12)
O1—C6—C5	109.8 (5)	C6—C16—C15	107.4 (7)
O1—C6—C16	97.4 (5)	C6—C16*A*—C15*A*	109.6 (14)
O1—C6—C16*A*	127.2 (9)	S—C19—C20	121.3 (5)
O7—C6—C5	106.3 (6)	S—C19—C24	118.6 (5)
O7—C6—C16	110.6 (5)	C20—C19—C24	120.0 (6)
O7—C6—C16*A*	109.7 (9)	C19—C20—C21	119.8 (7)
C5—C6—C16	122.2 (7)	C20—C21—C22	120.2 (7)
C5—C6—C16*A*	90.5 (9)	C21—C22—C23	119.6 (7)
O7—C8—O9	112.4 (4)	C22—C23—C24	120.5 (7)
O7—C8—C13	105.5 (4)	C19—C24—C23	119.7 (7)
O7—C8—C14	110.2 (5)		

The θ-scan width was $(0.80 + 0.33\tan\theta)^\circ$. Background measurements were extended by 25% of the peak scan on either side of each peak. The maximum time for measurement of one reflection was 60 s. Data collection and cell refinement: Enraf-Nonius (1984) *CAD*-4 *PDP*11 *Software*. Data reduction: *NRCVAX DATRD*2 (Gabe, Le Page, Charland, Lee & White, 1989). Program used to solve structure: *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Software used to prepare material for publication: *NRCVAX TABLES*; *ORTEP*II (Johnson, 1976). Program used to refine structure: *NRCVAX LSTSQ*. Block-diagonal least-squares refinement was performed, with H atoms included in their calculated positions, but not refined. Isotropic *U* values were assigned to the H atoms as equal to U_{eq} of the attached atom plus 0.010 Å^2. C15 and C16 of the central ring, along with their attached H atoms, were found to be disordered, with site occupancy factors of 0.65 and 0.35 for the major and minor conformers, respectively. Relative amounts of the two forms were determined by refining the population parameters of C15, C16, C15*A* and C16*A*, while holding the temperature factors constant. C15, C16, C15*A* and C16*A* were given isotropic thermal parameters during refinement; all other non-H atoms were given anisotropic thermal parameters. In the final refinement, the population parameters for C15, C16, H151, H152, H161 and H162 were set at 0.65 and the population parameters for C15*A*, C16*A*, H153, H154, H163 and H164 were set at 0.35.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71275 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1033]

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Structures of Two Hexacyclic Cage Diketone Monoacetals

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Abstract

The structures of 10,10-(ethylenedioxy)hexacyclo-[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-5,7-dien-3-one and 10,10-diisopropoxyhexacyclo[10.2.1.0^{2,11}.0^{4,9}.-0^{4,14}.0^{9,13}]pentadeca-5,7-dien-3-one are reported. In each structure the cyclohexadiene ring is planar. Bonding geometries are similar to those found in other cage structures, except for elongations of the

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