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4-Sulfonyl-1,6-dioxaspiro[4.5]decanes

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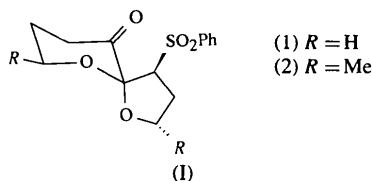
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Abstract

The relative configurations of 4-(phenylsulfonyl)-1,6-dioxaspiro[4.5]decan-10-one ($C_{14}H_{16}O_5S$) and its 2,7-dimethyl derivative, 2,7-dimethyl-4-(phenylsulfonyl)-1,6-dioxaspiro[4.5]decan-10-one ($C_{16}H_{20}O_5S$), are confirmed.

Comment

Since the spiroketal unit is found in a wide variety of natural products (Mishima *et al.*, 1975; Kato & Scheuer, 1974), considerable attention has been focused on the development of methods for the synthesis of this moiety (Perron & Albizati, 1989). Most of these methods are based on the thermodynamically controlled acid-catalysed spiroketalization of dihydroxyketones. However, recently, some one-step convergent syntheses from two fragments have been described (Gosselin, Bonfand, Hayes & Maignan, 1994; Ann & Cohen, 1994; Boons, Downham, Kim, Ley & Woods, 1994; Carretero, Díaz & Rojo, 1994).



The structures, with the atomic numbering schemes, of the title compounds (1) and (2) are shown in Figs. 1 and 2. The non-aromatic six-membered ring has a distorted-chair conformation which is slightly flattened around the carbonyl group. This effect is greater for compound (1) [torsion angle $C8-C9-C10-C5$ $35.5(6)$ in (1) and $46.3(3)^\circ$ in (2)]. The five-membered ring conformation is slightly different in these two compounds. In (1), the ring has an envelope conformation

with $C4$ (-0.53 \AA) out of the plane defined by $O1$, $C2$, $C3$ and $C5$, whereas in (2) the ring has a half-envelope conformation with $C3$ (-0.35 \AA) and $C4$ (0.28 \AA) out of the plane defined by the other three atoms. The shortening of the $C5-O1$ and $C5-O6$ bond distances and the geometrical disposition of these groups (both in axial positions) are similar in the two compounds, probably to maximize the thermodynamic anomeric effect (Deslongchamps, Rowan, Pothier, Sauvé & Saunders, 1981). The sulfone group is in a pseudo-equatorial position in both compounds. In (2), the methyl groups $C21$ and $C71$ are in pseudo-axial and equatorial positions, respectively. The most significant difference is the conformation around the $C4-S1$ bond [torsion angle $C5-C4-S1-C11$ $-42.4(4)$ in (1) and $70.5(2)^\circ$ in (2)].

Each molecule is involved in one hydrogen bond. In (1), $C14-H14 \cdots O12^i = 2.490(6)$, $C14 \cdots O12^i = 3.408(6) \text{ \AA}$ and $C14-H14 \cdots O12^i = 169.3(1)^\circ$ [symmetry code: (i) $x, y + 1, z$]; in (2), $C4-H4 \cdots O10^{ii} = 2.550(3)$, $C4 \cdots O10^{ii} = 3.401(3) \text{ \AA}$ and $C4-H4 \cdots O10^{ii} = 145.1(1)^\circ$ [symmetry code: (ii) $1 - x, 1 - y, 2 - z$].

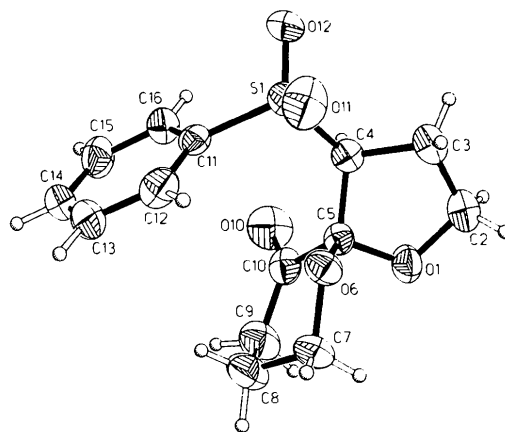


Fig. 1. Molecular structure of (1) showing 50% probability displacement ellipsoids.

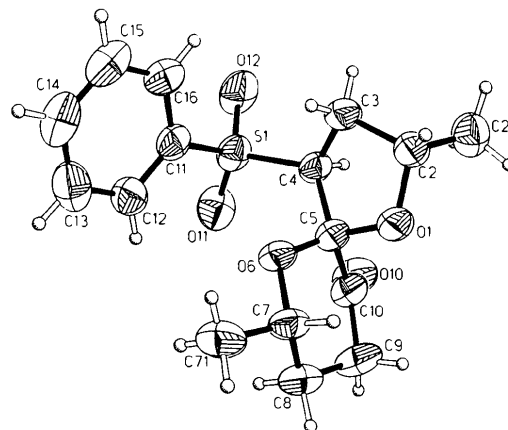


Fig. 2. Molecular structure of (2) showing 50% probability displacement ellipsoids.

Experimental

Crystals of (1) and (2) were grown by slow evaporation from an acetone solution of the compound placed in a bath of toluene (Carretero, Rojo, Díaz, Hamdouchi & Poveda, 1995).

C11	0.2335 (4)	1.1293 (5)	0.1372 (3)	0.0335 (11)
C12	0.3353 (5)	1.2328 (6)	0.1633 (3)	0.0484 (13)
C13	0.3108 (6)	1.3913 (6)	0.1460 (3)	0.0597 (15)
C14	0.1868 (6)	1.4431 (6)	0.1057 (3)	0.0600 (15)
C15	0.0852 (5)	1.3391 (6)	0.0802 (3)	0.0540 (14)
C16	0.1076 (4)	1.1798 (5)	0.0954 (3)	0.0431 (12)

Compound (1)

Crystal data

C ₁₄ H ₁₆ O ₅ S	Mo K α radiation
$M_r = 296.33$	$\lambda = 0.71073 \text{ \AA}$
Monoclinic	Cell parameters from 25 reflections
$P2_1/c$	$\theta = 7-16^\circ$
$a = 10.832 (2) \text{ \AA}$	$\mu = 0.253 \text{ mm}^{-1}$
$b = 8.524 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 15.634 (3) \text{ \AA}$	Transparent block
$\beta = 108.31 (3)^\circ$	$0.30 \times 0.28 \times 0.27 \text{ mm}$
$V = 1370.4 (5) \text{ \AA}^3$	Colourless
$Z = 4$	
$D_x = 1.436 \text{ Mg m}^{-3}$	

Data collection

Rigaku AFC-7 four-circle-diffractometer	$R_{\text{int}} = 0.0227$
$2\theta/\omega$ scans	$\theta_{\text{max}} = 22.50^\circ$
Absorption correction: none	$h = -11 \rightarrow 11$
1872 measured reflections	$k = 0 \rightarrow 9$
1791 independent reflections	$l = 0 \rightarrow 16$
1155 observed reflections [$I > 2\sigma(I)$]	3 standard reflections monitored every 100 reflections
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0496$	$\Delta\rho_{\text{max}} = 0.194 \text{ e \AA}^{-3}$
$wR(F^2) = 0.1037$	$\Delta\rho_{\text{min}} = -0.228 \text{ e \AA}^{-3}$
$S = 1.081$	Extinction correction: none
1790 reflections	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)
181 parameters	
Only coordinates of H atoms refined	
$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 0.8724P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (1)

	x	y	z	U_{eq}
O1	0.2412 (3)	0.9142 (3)	0.4092 (2)	0.0471 (9)
C2	0.2535 (5)	0.7499 (6)	0.3936 (3)	0.0578 (14)
C3	0.2660 (4)	0.7316 (5)	0.3010 (3)	0.0461 (11)
C4	0.2109 (4)	0.8870 (5)	0.2563 (3)	0.0350 (11)
C5	0.2482 (4)	1.0025 (5)	0.3345 (3)	0.0335 (10)
O6	0.3758 (2)	1.0550 (3)	0.3471 (2)	0.0395 (8)
C7	0.4238 (4)	1.1659 (5)	0.4199 (3)	0.0508 (13)
C8	0.3455 (5)	1.3133 (6)	0.4004 (4)	0.0609 (15)
C9	0.2044 (5)	1.2791 (6)	0.3871 (4)	0.064 (2)
C10	0.1542 (5)	1.1402 (5)	0.3278 (3)	0.0427 (12)
O10	0.0435 (3)	1.1293 (4)	0.2777 (2)	0.0677 (11)
S1	0.26055 (12)	0.92700 (13)	0.15903 (8)	0.0414 (4)
O11	0.3975 (3)	0.8972 (4)	0.1800 (2)	0.0626 (10)
O12	0.1716 (3)	0.8414 (4)	0.0863 (2)	0.0616 (10)

Table 2. Selected geometric parameters (\AA , $^\circ$) for (1)

O1—C5	1.411 (5)	O6—C7	1.445 (5)
O1—C2	1.435 (5)	C7—C8	1.493 (6)
C2—C3	1.504 (6)	C8—C9	1.505 (7)
C3—C4	1.529 (6)	C9—C10	1.496 (7)
C4—C5	1.523 (6)	C10—O10	1.213 (5)
C4—S1	1.797 (4)	S1—O12	1.437 (3)
C5—O6	1.407 (5)	S1—O11	1.438 (3)
C5—C10	1.536 (6)	S1—C11	1.764 (4)
C5—O1—C2	110.4 (3)	C7—C8—C9	110.7 (4)
O1—C2—C3	107.8 (4)	C10—C9—C8	113.2 (4)
C2—C3—C4	102.1 (4)	O10—C10—C9	123.6 (4)
C5—C4—C3	103.0 (3)	O10—C10—C5	119.0 (4)
C5—C4—S1	118.9 (3)	C9—C10—C5	117.3 (4)
C3—C4—S1	112.0 (3)	O12—S1—O11	118.6 (2)
O6—C5—O1	111.1 (3)	O12—S1—C11	108.3 (2)
O6—C5—C4	108.6 (3)	O11—S1—C11	108.3 (2)
O1—C5—C4	104.5 (3)	O12—S1—C4	105.6 (2)
O6—C5—C10	111.5 (3)	O11—S1—C4	109.6 (2)
O1—C5—C10	104.9 (3)	C11—S1—C4	105.9 (2)
C4—C5—C10	115.9 (4)	C12—C11—S1	120.2 (3)
C5—O6—C7	114.3 (3)	C16—C11—S1	118.4 (3)
O6—C7—C8	110.4 (4)		

Compound (2)

Crystal data

C ₁₆ H ₂₀ O ₅ S	Cu K α radiation
$M_r = 324.38$	$\lambda = 1.54178 \text{ \AA}$
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	$\theta = 20-25^\circ$
$a = 8.613 (2) \text{ \AA}$	$\mu = 2.008 \text{ mm}^{-1}$
$b = 10.453 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 10.561 (2) \text{ \AA}$	Transparent block
$\alpha = 63.55 (3)^\circ$	$0.30 \times 0.28 \times 0.25 \text{ mm}$
$\beta = 68.81 (3)^\circ$	Colourless
$\gamma = 84.74 (3)^\circ$	
$V = 791.0 (3) \text{ \AA}^3$	
$Z = 2$	
$D_x = 1.362 \text{ Mg m}^{-3}$	

Data collection

Rigaku AFC-7 four-circle-diffractometer	$R_{\text{int}} = 0.0188$
$2\theta/\omega$ scans	$\theta_{\text{max}} = 76.78^\circ$
Absorption correction: none	$h = -10 \rightarrow 10$
3113 measured reflections	$k = -10 \rightarrow 0$
2937 independent reflections	$l = -13 \rightarrow 10$
2659 observed reflections [$I > 2\sigma(I)$]	3 standard reflections monitored every 100 reflections
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.064$
$R[F^2 > 2\sigma(F^2)] = 0.0427$	$\Delta\rho_{\text{max}} = 0.189 \text{ e \AA}^{-3}$
$wR(F^2) = 0.1199$	$\Delta\rho_{\text{min}} = -0.512 \text{ e \AA}^{-3}$
$S = 1.077$	Extinction correction: none

2937 reflections
199 parameters
Only coordinates of H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0650P)^2 + 0.2606P]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

We thank the SERC for funding for the AFC-7 diffractometer, the DGICYT for a grant to ILS and Europharma for a grant to IA. We also thank Nuria Díaz for preparing the crystals of these compounds.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
S1	0.70131 (6)	0.30295 (6)	0.83579 (6)	0.0533 (2)
O11	0.6243 (2)	0.1883 (2)	0.9845 (2)	0.0736 (5)
O12	0.8506 (2)	0.3819 (2)	0.8028 (2)	0.0766 (5)
C3	0.6044 (2)	0.5542 (2)	0.6399 (2)	0.0520 (5)
C2	0.4418 (2)	0.6274 (2)	0.6451 (2)	0.0510 (5)
C21	0.4235 (3)	0.7428 (3)	0.6968 (3)	0.0678 (6)
O1	0.3113 (2)	0.51281 (15)	0.7520 (2)	0.0601 (4)
C5	0.3758 (2)	0.3874 (2)	0.8366 (2)	0.0470 (4)
C4	0.5551 (2)	0.4349 (2)	0.8014 (2)	0.0459 (4)
O6	0.37838 (14)	0.28125 (14)	0.78863 (14)	0.0475 (3)
C7	0.2149 (2)	0.2337 (2)	0.8058 (2)	0.0510 (5)
C71	0.2448 (3)	0.1265 (3)	0.7414 (3)	0.0661 (6)
C8	0.1040 (2)	0.1696 (3)	0.9711 (2)	0.0594 (5)
C9	0.0887 (3)	0.2756 (3)	1.0360 (3)	0.0711 (7)
C10	0.2573 (2)	0.3379 (2)	1.0018 (2)	0.0557 (5)
O10	0.2993 (2)	0.3512 (2)	1.0930 (2)	0.0741 (5)
C11	0.7522 (2)	0.2317 (2)	0.7038 (2)	0.0508 (5)
C12	0.6806 (3)	0.0986 (2)	0.7477 (3)	0.0601 (5)
C13	0.7329 (4)	0.0394 (3)	0.6460 (3)	0.0769 (7)
C14	0.8517 (3)	0.1131 (3)	0.5040 (3)	0.0769 (7)
C15	0.9215 (3)	0.2453 (3)	0.4611 (3)	0.0771 (7)
C16	0.8732 (3)	0.3046 (3)	0.5611 (3)	0.0638 (6)

Table 4. Selected geometric parameters (\AA , $^\circ$) for (2)

S1—O11	1.435 (2)	C5—O6	1.406 (2)
S1—O12	1.439 (2)	C5—C4	1.527 (2)
S1—C11	1.765 (2)	C5—C10	1.536 (3)
S1—C4	1.785 (2)	O6—C7	1.458 (2)
C3—C4	1.524 (3)	C7—C8	1.510 (3)
C3—C2	1.528 (3)	C7—C71	1.511 (3)
C2—O1	1.449 (2)	C8—C9	1.516 (3)
C2—C21	1.506 (3)	C9—C10	1.499 (3)
O1—C5	1.417 (2)	C10—O10	1.207 (3)
O11—S1—O12	119.08 (12)	C4—C5—C10	115.8 (2)
O11—S1—C11	108.05 (10)	C3—C4—C5	102.70 (15)
O12—S1—C11	106.49 (10)	C3—C4—S1	115.85 (13)
O11—S1—C4	108.28 (10)	C5—C4—S1	119.20 (14)
O12—S1—C4	104.53 (10)	C5—O6—C7	114.59 (14)
C11—S1—C4	110.24 (9)	O6—C7—C8	109.4 (2)
C4—C3—C2	101.3 (2)	O6—C7—C71	106.5 (2)
O1—C2—C21	109.5 (2)	C8—C7—C71	112.5 (2)
O1—C2—C3	104.5 (2)	C7—C8—C9	111.2 (2)
C21—C2—C3	114.2 (2)	C10—C9—C8	111.2 (2)
C5—O1—C2	111.61 (14)	O10—C10—C9	124.4 (2)
O6—C5—O1	111.0 (2)	O10—C10—C5	121.5 (2)
O6—C5—C4	108.99 (14)	C9—C10—C5	114.1 (2)
O1—C5—C4	104.85 (15)	C12—C11—S1	119.5 (2)
O6—C5—C10	111.0 (2)	C16—C11—S1	119.7 (2)
O1—C5—C10	105.0 (2)		

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992b); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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9-(Carboxymethyl)-2,6-dichloropurine Ethyl Ester. An Intermediate for Peptidic Nucleic Acid Synthesis

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Abstract

The title compound (ethyl 2,6-dichloropurine-9-acetate, $C_9H_8Cl_2N_4O_2$) is an intermediate for the synthesis