

Hydrogen bonds and C—H···O interactions in the enol tautomer of 4-(phenylsulfonyl)spiro[cyclopentane-1,9'-[9*H*]fluorene]-2,3-dione

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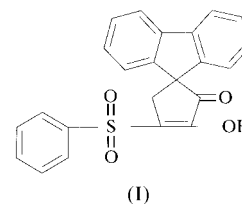
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The title compound, 2-hydroxy-1-(phenylsulfonyl)spiro[cyclopentene-4,9'-[9*H*]fluorene]-3-one, $C_{23}H_{16}O_4S$, crystallized in the centrosymmetric space group $P2_1/n$ with one molecule as the asymmetric unit. The hydroxyl-H atom is ordered and participates in a single intramolecular hydrogen bond and in a single intermolecular hydrogen bond, in which the O_D-H distance is 0.90 (2), $H\cdots O_A$ is 2.34 (3), $O_D\cdots O_A$ is 2.987 (2) Å and $O_D-H\cdots O_A$ is 129 (2)°. The intermolecular hydrogen bond forms an $R_2^2(12)$ cyclic dimer about a center of symmetry. There are six leading C—H···O interactions. Taken together, these interactions form a three-dimensional network. Structural comparisons are made with tetrabenzodispiro[4.0.4.3]-tridecatetraene.

Comment

This report on the title enol, (I), is one of a series on hydrogen bonding in organic solids, and the third structural report on a spirocyclopentyl-1,9'-[9*H*]fluorene compound. (I) crystallized in the centrosymmetric space group $P2_1/n$ with one molecule as the asymmetric unit. The refined molecule and the labeling scheme are shown in Fig. 1. The hydroxyl-H atom is ordered and participates in a single intramolecular hydrogen bond and in a single intermolecular hydrogen bond, the geometric parameters of which are given in Table 2. The intermolecular hydrogen bond forms a first-level (Bernstein *et al.*, 1995) cyclic dimer, with descriptor $R_2^2(12)$, about a center of symmetry. In addition, there are six leading C—H···O interactions (Taylor & Kennard, 1982; Steiner & Desiraju, 1998) whose parameters are also given in Table 2. Each molecule is linked directly by these interactions to eleven neighbors. The results of basic first- and second-level graph-set analysis involving all of these interactions, labeled *a–h* for this purpose in the order of their appearance in Table 2, are given in Table 3. The dominant patterns are rings (8) and chains (26). The chains propagate variously along [100] (6), [010] (10), [10 $\bar{1}$] (4), [101] (3), [210] (2) and [1 $\bar{1}$ 0], and generate a richly three-dimensional network of interactions. It may be noted that, if only those C—H···O

interactions having an $H\cdots O$ distance less than the corresponding Bondi (1964) van der Waals radius sum are considered, the resulting interaction network remains three-dimensional. A packing stereodiagram of the structure is given in Fig. 2.



As for the fluorene cores in fluorene carboxylic acids (Blackburn *et al.*, 1996), best-fit planes for atoms C1–C4, C10 and C11 and atoms C5–C8, C12 and C13 have been chosen to define the fluorene core dihedral angle in (I). The maximum distance of any of these atoms from the best-fit plane including that atom is 0.007 (2) Å, and the dihedral angle is 2.10 (10)°. For structural comparisons, tetrabenzodispiro[4.0.4.3]-tridecatetraene [hereafter, (II)] (Fritze *et al.*, 1995), which can be viewed in the present context as a double spirocyclopentane-1,9'-[9*H*]fluorene, is particularly appropriate. In (II), there are four independent fluorene cores and for them the maximum deviation of an atom from the corresponding best-fit planes is 0.023 (3) Å, and the dihedral angles are 10.60 (11), 9.19 (8), 8.32 (10) and 6.68 (9)°, all considerably larger than in (I). The central ring of the fluorene core is less nearly planar than the outer rings in (I), the maximum atom deviation from the best-fit plane being 0.018 (2) Å; for (II), the quite similar corresponding values are 0.025 (2), 0.022 (2), 0.027 (2) and 0.020 (2) Å. A second notable difference between (I) and (II) is that the cyclopentyl ring has a 0.033 (2) Å maximum atom deviation from the best-fit plane in (I), but 0.245 (2) and 0.225 (2) Å in (II). A further similarity of (I) and (II) is that the dihedral angles between the best-fit planes describing the spiro-connected five-membered rings are, as expected, close to 90°, being 89.95 (10)° in (I) and 89.67 (10), 88.68 (9),

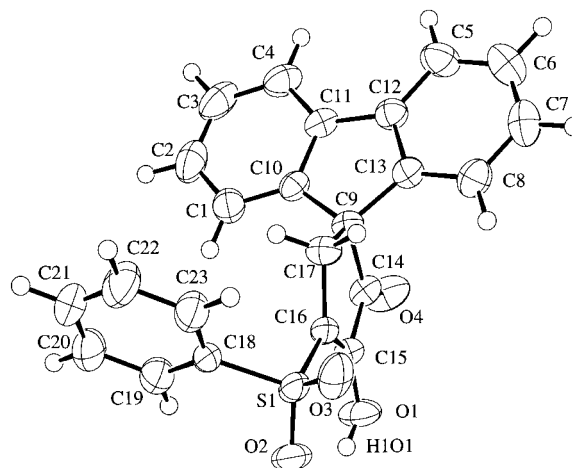


Figure 1
Labeling scheme for (I) with displacement ellipsoids at the 50% probability level.

89.46 (10) and 90.00 (10)° in (II). For the phenyl ring of (I), C18–C23, the maximum deviation of an atom from the best-fit plane describing them is 0.004 (2) Å.

Selected distances and angles for (I) are given in Table 1. All distances and angles fall within normal ranges. The r.m.s. deviation within the seven pairs of chemically equivalent bond distances in the fluorene core is 0.006 Å for (I), while for the four cores in (II) it is 0.007, 0.002, 0.006 and 0.006 Å. Overall, the mean values of the seven chemically equivalent bond distances in the fluorene core of (I) are in good agreement with the corresponding seven grand mean values for the four fluorene cores of (II): C4–C11, 1.388 (2) versus 1.392 (3); C3–C4, 1.378 (3) versus 1.375 (5); C2–C3, 1.374 (3) versus 1.379 (6); C1–C2, 1.388 (3) versus 1.391 (4); C1–C10, 1.380 (2) versus 1.386 (4); C10–C11, 1.394 (2) versus 1.399 (3); and C9–C10, 1.520 (5) versus 1.525 (3) Å. The bond distance for the unique bond of the fluorene core, C11–C12, is 1.460 (2) Å for (I), 1.462 (3) Å (grand mean) for (II). Excluding pairs of atoms in hydrogen-bonded groups or tabulated C–H···O interactions, the closest intermolecular approaches are between C1 and H17B^{vii} [symmetry code: (vii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$], and are 0.01 Å less than the corresponding Bondi (1964) van der Waals radius sum.

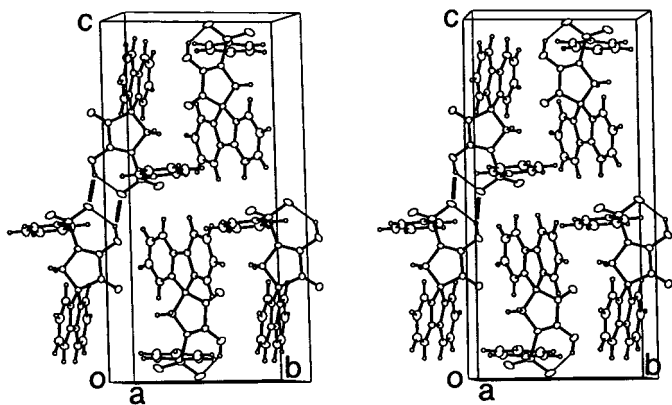


Figure 2 Packing stereodiagram of (I). The finer interatomic lines depict the intramolecular hydrogen bonds.

Experimental

The title compound was obtained as a colorless plate from a coarsely crystalline sample in Dr M. S. Newman's chemical collection. The experimental sample was cut from this plate. A synthesis of (I) is described by Newman (1984).

Crystal data

C₂₃H₁₆O₄S
M_r = 388.44
 Monoclinic, *P*2₁/*n*
a = 8.478 (1) Å
b = 10.406 (1) Å
c = 21.336 (1) Å
 β = 95.701 (9)°
V = 1873.2 (4) Å³
Z = 4

D_x = 1.377 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 16.1–17.5°
 μ = 0.200 mm⁻¹
T = 296 K
 Cut plate, colorless
 0.42 × 0.35 × 0.27 mm

Table 1 Selected geometric parameters (Å, °).

S1–O2	1.4462 (13)	C9–C14	1.536 (2)
S1–O3	1.4358 (14)	C9–C17	1.549 (2)
S1–C16	1.742 (2)	C14–C15	1.488 (2)
S1–C18	1.759 (2)	C15–C16	1.332 (2)
O1–C15	1.333 (2)	C16–C17	1.503 (2)
O4–C14	1.201 (2)		
O2–S1–O3	118.96 (8)	C14–C9–C17	104.70 (13)
O2–S1–C16	106.50 (8)	O4–C14–C9	126.8 (2)
O2–S1–C18	109.26 (8)	O4–C14–C15	125.7 (2)
O3–S1–C16	109.44 (8)	C9–C14–C15	107.51 (14)
O3–S1–C18	108.63 (9)	O1–C15–C14	117.6 (2)
C16–S1–C18	102.85 (8)	O1–C15–C16	132.9 (2)
C10–C9–C13	101.83 (13)	C14–C15–C16	109.53 (15)
C10–C9–C14	109.41 (14)	S1–C16–C15	124.75 (13)
C10–C9–C17	114.39 (14)	S1–C16–C17	121.25 (13)
C13–C9–C14	110.53 (14)	C15–C16–C17	114.00 (14)
C13–C9–C17	116.01 (14)	C9–C17–C16	104.02 (14)

Data collection

AFC-5S diffractometer
 ω scans
 4618 measured reflections
 4333 independent reflections
 3246 reflections with *I* > 2.0 σ _{*I*}
*R*_{int} = 0.010
 θ _{max} = 27.55°

h = 0 → 11
k = 0 → 13
l = -27 → 27
 6 standard reflections every 150 reflections
 intensity decay: -1.8%

Refinement

Refinement on *F*²
R(*F*) = 0.046
wR(*F*²) = 0.083
S = 1.44
 4331 reflections
 257 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma_{cs}^2 + (0.012I)^2]$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.39 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.47 \text{ e } \text{Å}^{-3}$

Table 2 Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1–H1O1···O2	0.90 (2)	2.11 (2)	2.836 (2)	137 (2)
O1–H1O1···O2 ⁱ	0.90 (2)	2.34 (3)	2.987 (2)	129 (2)
C7–H7···O4 ⁱⁱ	0.98	2.47	3.407 (3)	161
C17–H17A···O4 ⁱⁱⁱ	0.98	2.66	3.413 (2)	134
C4–H4···O3 ^{iv}	0.98	2.67	3.351 (2)	127
C21–H21···O3 ^v	0.98	2.67	3.528 (3)	146
C7–H7···O1 ⁱⁱ	0.98	2.81	3.572 (3)	135
C6–H6···O2 ^{vi}	0.98	2.84	3.816 (2)	179

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $1 + x, y, z$; (vi) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$.

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

Table 3Basic first- and second-level graph-set descriptors involving interactions designated *a–h* in the order given in Table 2.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>
<i>a</i>	$S(6)$	$D_2^2(6)$	$C_2^2(15)[S(6)]$	$C_2^2(10)[S(6)]$	$R_4^4(24)[S(6)]$	$C_2^2(13)[S(6)]$	$C_2^2(11)[S(6)]$	$C_2^1(11)[S(6)]$
<i>b</i>		$R_2^2(12)$	$C_2^2(14)$	$C_2^2(10)$	$C_2^2(12)$	$C_2^2(13)$	$C_2^2(11)$	$C_2^1(11)$
<i>c</i>			$C(7)$	$C_2^1(8)$	$R_4^4(28)$	$C_2^2(19)$	$C_2^1(7)[R_1^1(5)]$	$R_4^4(20)$
<i>d</i>				$C(5)$	$R_4^4(24)$	$C_2^2(15)$	$C_2^2(12)$	$R_4^4(20)$
<i>e</i>					$C(9)$	$C_2^1(14)$	$R_4^4(26)$	$C_2^2(10)$
<i>f</i>						$C(7)$	$C_2^2(18)$	$C_2^2(17)$
<i>g</i>							$C(8)$	$R_4^4(18)$
<i>h</i>								$C(10)$

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1267). Services for accessing these data are described at the back of the journal.

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