

A novel chelatofore functionalized
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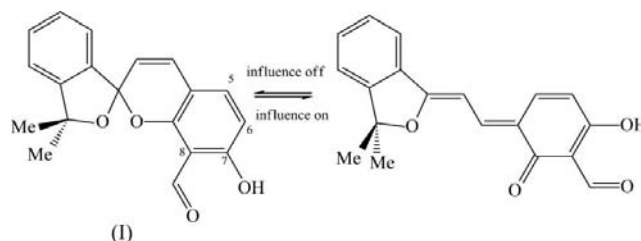
A novel chelatofore functionalized spiropyran of the 2-oxaindane series, namely 8-formyl-7-hydroxy-3',3'-dimethyl-spiro[2*H*-chromene-2,1'(3'*H*)-2-benzofuran], C₁₉H₁₆O₄, is reported. In the crystalline state, dimers are formed as a result of the π - π stacking of aromatic groups of the 2*H*-chromene part of the molecule and C—H...O interactions. The C_{spiro}—O bond length in the pyran ring is 1.4558 (10) Å, which is longer than or equal to the bond length in thermo- and photochromic 2-oxaindane spiropyran synthesized previously, except for the 7,8-benzo/6-NO₂ derivative, in which this bond length is 1.465 (2) Å.

Comment

Heterocyclic spiropyran are a class of substances which can possess photo- (Bertleson, 1971; Durr, 1990), electro- (Monk *et al.*, 1995) and thermochromic (Bercovic *et al.*, 2000) properties as a result of reversible opening–closing reactions of the pyran ring (see scheme) under the effect of light, external electric field or heat, respectively. The number of studies of this class of substances is steadily growing, and their syntheses (Lukyanov & Lukyanova, 2005) and properties (Minkin, 2004) have been thoroughly summarized and reviewed. One of the challenging goals in this field is to develop synthetic methods of functionalization of molecules with photochromic properties (*e.g.* the spiropyran class) by incorporating into their structure chelating groups in order to prepare coordination compounds with transition and *f*-block metal ions; such an approach will allow us to study the possibility of tuning the photochromic properties of the spiropyran unit by complex formation and obtaining promising hybrid photo- and magnetoactive substances (Bulanov *et al.*, 2002, 2003).

We present here the crystal structure of a novel spiropyran of the 2-oxaindane series, 8-formyl-7-hydroxy-3',3'-dimethyl-spiro[2*H*-chromene-2,1'(3'*H*)-2-benzofuran], (I), which is functionalized by chelatofore centres (with the hydroxy

group in a position *ortho* to the formyl group) for further synthesis of novel ligand systems (Schiff bases, hydrazones, *etc.*). The numbering of the atoms for (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1.



The title compound crystallizes in the closed spiro form. The main features of the molecular structure are similar to spiropyran studied so far. In the molecule of (I), the 2*H*-chromene and oxaindane fragments are nearly orthogonal to each other [the angle between the least-squares planes is 85.74 (3)°]. The pyran and oxaindane rings joined at spiro-centre C2 are substantially nonplanar. The oxaindane ring is in the 'envelope' conformation, with atom O2' lying 0.123 (1) Å out of the least-squares plane defined by the other eight non-H atoms of this fragment [the largest deviation from the least-squares plane within this group is 0.026 (1) Å] as a result of bending along the C2...C1' line. In the substituted benzopyran fragment, 11 atoms (all except spiro-atom C2 and pyran atom O1) are located in one plane; the largest deviation is 0.033 (1) Å. The pyran ring is distorted as a result of a small (for a six-membered ring) bond angle at the *sp*³-hybridized atom C2 [112.44 (7)°]. Atoms O1 and C2 deviate on opposite sides of the aforementioned least-squares plane by 0.122 (1) and 0.212 (1) Å, respectively. The pyran ring is bent in such a way that atom O2' of the oxaindane ring is closer to the plane of the pyran ring. This conformation favours the conjugation between the lone pair of atom O2' and the antibonding σ orbital of the C2—O1 bond in the pyran ring, analogous to the situation found in benzoxazinone (Bulanov *et al.*, 2008) and other series (Minkin, 2004) of spiropyran. The characteristics

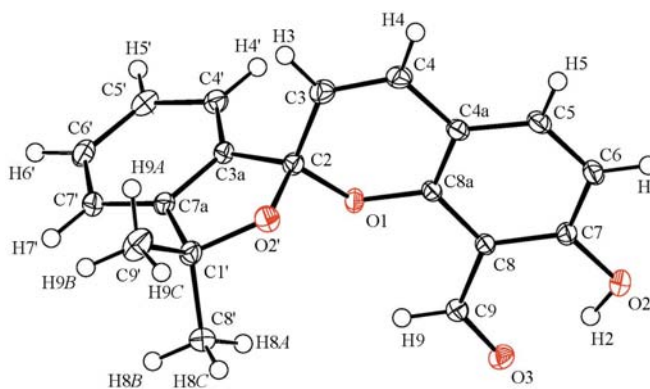


Figure 1
The crystal structure of (I), showing the atom-numbering scheme used in the *Comment*. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.

of the strong intramolecular hydrogen bond formed between neighbouring 7-OH and 8-formyl groups are given in Table 2.

It is interesting to compare the structural parameters of (I) with those of other previously studied representatives of the 2-oxaindane series, to evaluate the influence of incorporated chelator groups on the properties of the spirocentre. In the Cambridge Structural Database (Version 5.30, plus September 2009 updates; Allen, 2002), the crystal structures of five spiroopyrans of this series determined by single-crystal X-ray diffraction are reported. A comparison of some geometric parameters is presented in Table 3. Of special interest in the spiroopyran molecules is the length of the $C_{\text{spiro}}-\text{O}$ bond in the pyran ring [C2—O1 in (I)], which is strongly correlated with the possibility of the opening–closing of the pyran ring reaction under internal influence. The longer this bond is, the weaker it is, and thus, at least, thermoactivation of the bond is easier. It can be seen that in (I) this bond is 1.4558 (10) Å and it is the second longest bond in this series; it is even longer than in the case of the 6-NO₂ substituent, indicating that the effect of the π -acceptor 8-formyl and π -donor 7-OH groups is synergetic and leads to activation of the $C_{\text{spiro}}-\text{O}$ bond. This is a promising result if we have in mind further synthesis of such ligands and their metal complexes. Thus, it can be proposed that functionalization of the parent spiroopyran of the oxaindane family with chelator groups will not influence its photochromic properties. From the data in Table 3 it is also seen that elongation of the active bond correlates rather well with shortening of the C8A—O1 and C2—O2' bonds.

In the crystal structure of (I), the formation of centrosymmetric dimers due to strong $\pi-\pi$ and C—H...O interactions (see Fig. 2 and Table 2) is observed. The stacking interaction is implemented through the π systems of the aromatic rings of the 2H-chromene units of two molecules that are arranged strictly parallel to each other at a distance of 3.3002 (4) Å in such a way that the C atom of the formyl substituent of one molecule (C9) is close to atom C5ⁱ of the counterpart molecule [3.3843 (13) Å] and atom C7 is close to C8Aⁱ [3.2964 (12) Å] and *vice versa* [symmetry code: (i) $-x + 1, -y + 1, -z + 1$]. The distance between the centroids of the rings is 3.6095 (5) Å,

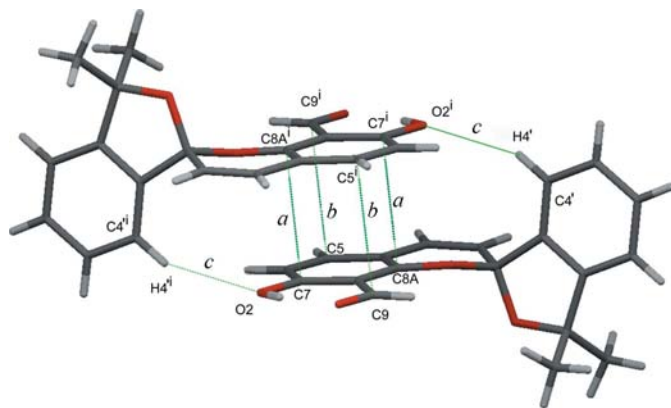


Figure 2
Close contacts in dimers of (I): (a) 3.2964 (12) Å, (b) 3.3843 (13) Å and (c) 2.46 Å. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

which corresponds to a 1.462 Å relative shift of the molecules along the C8—C9 bond. Atoms C7, C5, C8A and C9 of both molecules form a polyhedron, which is very close to a right-angle prism. An additional co-operative effect in the stabilization of the dimers is achieved *via* hydrogen bonding of the C4'—H4' bond of one molecule with the hydroxy O atom of another molecule. The interatomic C4'—H4'...O2ⁱ distance is 2.46 Å, indicating a significant interaction (see Table 2).

Dimers are interconnected by a weaker $\pi-\pi$ stacking interaction between the aromatic ring of the benzopyran unit and the aromatic ring of the oxaindane fragment in the symmetry-related molecule at $(x, \frac{3}{2} - y, \frac{1}{2} + z)$. The angle between the planes of the aromatic rings is 9.61 (4)°, the distance between the ring centroids is 3.6804 (5) Å, the perpendicular distance of the benzopyran aromatic ring from the oxaindane aromatic ring is 3.2746 (4) Å, and the perpendicular distance of the oxaindane aromatic ring from the benzopyran aromatic ring is 3.4581 (4) Å.

Experimental

The synthesis of (I) was performed in three successive steps. First, 1-oxy-1,3,3-trimethylphthalane, (II), was synthesized according to the method described by Fabrycy (1960). Condensation of (II) with 2,4-dihydroxyisophthalaldehyde was performed in a 1:1 (v/v) mixture of acetic acid and acetic anhydride in the presence of HClO₄ (yield 23%). The obtained 1-(2-oxystyryl)-3,3-dimethoxynaphthylisobenzofurylium perchlorate was dissolved in hexane and treated with gaseous NH₃ to give a yellow solution of (I). After evaporation of hexane, a yellow solid was obtained and recrystallized from ethanol (m.p. 379 K). Crystals suitable for X-ray diffraction were obtained by slow evaporation from a benzene solution.

Crystal data

$C_{19}H_{16}O_4$	$V = 1528.76$ (11) Å ³
$M_r = 308.32$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.1470$ (4) Å	$\mu = 0.09$ mm ⁻¹
$b = 11.1289$ (4) Å	$T = 100$ K
$c = 15.2605$ (6) Å	$0.24 \times 0.21 \times 0.18$ mm
$\beta = 100.231$ (1)°	

Data collection

Bruker SMART APEXII CCD	20124 measured reflections
area-detector diffractometer	4637 independent reflections
Absorption correction: multi-scan	3978 reflections with $I > 2\sigma(I)$
(SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.025$
$T_{\text{min}} = 0.979, T_{\text{max}} = 0.985$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	210 parameters
$wR(F^2) = 0.105$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.42$ e Å ⁻³
4637 reflections	$\Delta\rho_{\text{min}} = -0.24$ e Å ⁻³

The H atom of the hydroxy group was located in a difference Fourier synthesis. H atoms attached to C atoms were placed in calculated positions. All H atoms were refined in the isotropic approximation using an appropriate riding model, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}, \text{O})$ for methyl and hydroxy groups and $1.2U_{\text{eq}}(\text{C})$ for the aromatic H atoms.

Table 1

Selected geometric parameters (Å, °).

O1—C2	1.4558 (10)	C6—C7	1.3968 (13)
O1—C8A	1.3570 (10)	C7—O2	1.3487 (11)
C2—O2'	1.4185 (11)	C7—C8	1.4111 (11)
C1'—O2'	1.4614 (11)	C8—C8A	1.4088 (12)
C2—C3	1.4993 (12)	C8—C9	1.4512 (12)
C2—C3A	1.5044 (12)	C9—O3	1.2356 (11)
C3—C4	1.3355 (13)	C1'—C7A	1.5049 (12)
C4—C4A	1.4517 (12)	C1'—C9'	1.5196 (13)
C4A—C5	1.4029 (12)	C1'—C8'	1.5286 (13)
C5—C6	1.3824 (13)	C3A—C7A	1.3820 (12)
O1—C2—C3	112.44 (7)	C2—O2'—C1'	112.06 (7)
O2'—C2—C3A	104.81 (7)	O3—C9—C8	123.54 (8)
C8A—O1—C2	120.54 (7)	C7—O2—H2	103.9
C3—C4—C4A—C8A	5.64 (13)	C8A—C8—C9—O3	177.49 (8)

Table 2

Hydrogen-bond 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>
O2—H2···O3	0.91	1.75	2.5953 (10)	154
C4'—H4'···O2 ⁱ	0.95	2.46	3.3465 (11)	155

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 3

Comparison of selected geometric parameters (Å) of the 2-oxaindane series of spiropyrans.

<i>R</i>	<i>d</i> (C2—O1)	<i>d</i> (C2—O2')	<i>d</i> (C8A—O1)	Reference
6-NO ₂	1.454	1.409	1.365	Karaev <i>et al.</i> (1981)
7,8-benzo	1.4457 (7)	1.4156 (8)	1.372 (1)	Aldoshin <i>et al.</i> (1987)
7,8-benzo/6-Br	1.455 (3)	1.413 (5)	1.366 (4)	Aldoshin <i>et al.</i> (1987)
7,8-benzo/6-NO ₂	1.465 (2)	1.407 (3)	1.354 (3)	Aldoshin <i>et al.</i> (1987)
7,8-naphtho	1.448 (2)	1.416 (2)	1.377 (9)	Aldoshin <i>et al.</i> (1987)
7-OH/8-formyl	1.4558 (10)	1.4185 (11)	1.3570 (10)	This work, (I)

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to

refine structure: *SHELXTL*; molecular graphics: *Mercury* (Macrae *et al.*, 2006) and *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3023). Services for accessing these data are described at the back of the journal.

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