

## Novel hydrazone derivatives of 7-hydroxy-3',3'-dimethyl-3'*H*-spiro[chromene-2,1'-isobenzofuran]-8-carbaldehyde

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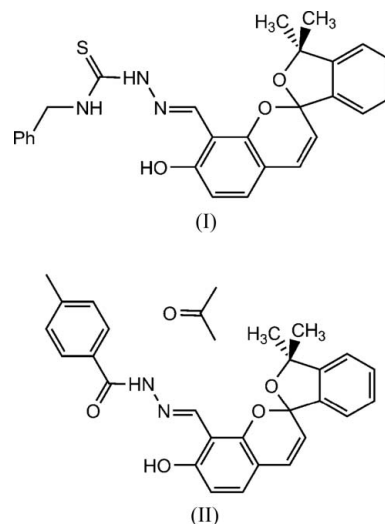
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The structures of new oxaindane spiropyrans derived from 7-hydroxy-3',3'-dimethyl-3'*H*-spiro[chromene-2,1'-isobenzofuran]-8-carbaldehyde (SP1), namely *N*-benzyl-2-[(7-hydroxy-3',3'-dimethyl-3'*H*-spiro[chromene-2,1'-isobenzofuran]-8-yl)methylidene]hydrazinecarbothioamide, C<sub>27</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub>S, (I), at 120 (2) K, and *N'*-[(7-hydroxy-3',3'-dimethyl-3'*H*-spiro[chromene-2,1'-isobenzofuran]-8-yl)methylidene]-4-methylbenzohydrazide acetone monosolvate, C<sub>27</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>·C<sub>3</sub>H<sub>6</sub>O, (II), at 100 (2) K, are reported. The photochromically active C<sub>spiro</sub>—O bond length in (I) is close to that in the parent compound (SP1), and in (II) it is shorter. In (I), centrosymmetric pairs of molecules are bound by two equivalent N—H···S hydrogen bonds, forming an eight-membered ring with two donors and two acceptors.

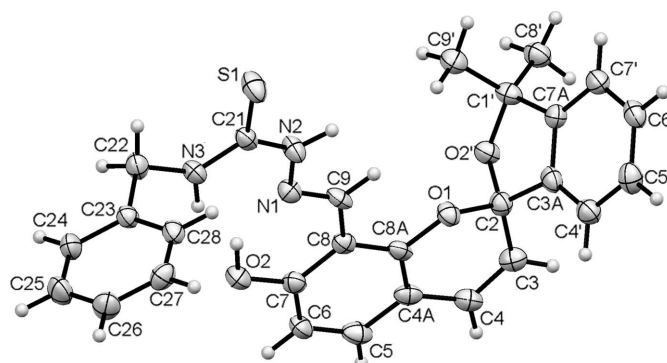
### Comment

The design and synthesis of multifunctional molecules, combining in their structure several active moieties, sensitive towards different external influences have attracted significant interest recently. One such example is photomagnetoactive substances capable of switching their magnetic properties under light irradiation. A promising development strategy in this direction is the synthesis of mono- or polynuclear transition or *f*-block metal complexes with photochromic organic molecules functionalized with chelate-forming centres. Heterocyclic spiropyrans of different series are potential substances which can possess photochromic properties as a result of reversible opening–closing reactions of the pyran ring under the effect of light (Bertleson, 1971; Durr, 1990; Minkin, 2004). This work extends our efforts in obtaining chelatore functionalized spiropyrans (Bulanov *et al.*, 2002, 2003, 2008, 2009).

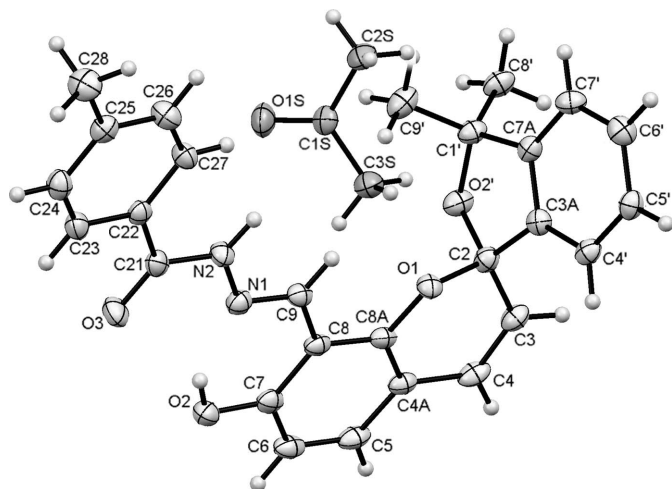
We present here the crystal structures of two novel hydrazone derivatives of the previously reported (Bulanov *et al.*, 2009) spiropyran of the 2-oxaindane series, 7-hydroxy-3',3'-dimethyl-3'*H*-spiro[chromene-2,1'-isobenzofuran]-8-carbaldehyde (hereafter referred to as SP1). *N*-Benzyl-2-[(7-hydroxy-3',3'-dimethyl-3'*H*-spiro[chromene-2,1'-isobenzofuran]-8-yl)methylidene]hydrazinecarbothioamide, (I), was obtained by a condensation reaction with *N*-benzylhydrazinecarbothioamide, and *N'*-[(7-hydroxy-3',3'-dimethyl-3'*H*-spiro[chromene-2,1'-isobenzofuran]-8-yl)methylidene]-4-methylbenzohydrazide acetone monosolvate, (II), was obtained in a similar manner with 4-methylbenzohydrazide. The atom-numbering schemes for (I) and (II) are shown in Figs. 1 and 2, respectively, and selected geometric parameters are given in Table 1.



Both compounds crystallize in the closed spiroform. The main features of the spiropyran fragment of both compounds are similar to those of the mother spiropyran, SP1, and other derivatives studied so far. The 2*H*-chromene and oxaindane fragments are nearly orthogonal to each other [the angle between the least-squares planes is 83.1 (2)° in (I) and 83.91 (13)° in (II)]. The pyran and oxaindane rings joined at the spirocentre C2 are substantially nonplanar. The oxaindane moiety is in the 'envelope' conformation with atom O2' at the apex out of the least-squares plane defined by the other non-H



**Figure 1**  
The crystal structure of (I), with displacement ellipsoids drawn at the 50% probability level.

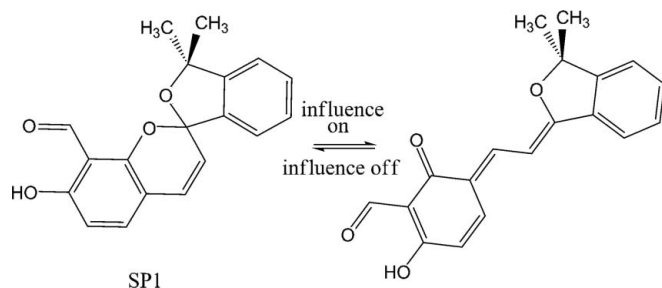


**Figure 2**  
The crystal structure of (II), with displacement ellipsoids drawn at the 50% probability level.

atoms of this fragment, *viz.* C1', C2, C3A, C4'–C7', C7A (due to bending along the C2...C1' line), by 0.247 (3) Å in (I) and 0.238 (2) Å in (II). The extent of the pyran ring distortion in both compounds is rather similar. The most significant deviation from the least-squares plane defined by the ten non-H atoms of the benzopyran fragments is found for the spiro C2 0.234 (4) Å in (I) and –0.241 (2) Å in (II)] and O1 atoms [0.155 (3) Å in (I) and 0.160 (2) Å in (II)]. The pyran ring is bent in such a way that the O2' atom of the oxindane moiety is closer to the plane of the pyran ring. This conformation favours the conjugation between the lone pair of atom O2' and the antibonding  $\sigma$  orbital of the C2–O1 bond in the pyran ring, analogous to benzoxazinone (Bulanov *et al.*, 2008) and other series (Minkin, 2004) of spiropyran.

In both compounds, strong intramolecular hydrogen bonds between neighbouring 7-OH and azomethine N atoms (O2–H2...N1) are observed; their geometric parameters are given in Tables 2 and 3. One more intramolecular hydrogen bond is present in (I) between the thioamide hydrogen and hydrazone N atoms, *viz.* N3–H3N...N1, which is involved in stabilization of the nearly planar configuration of the thiosemicarbazone moiety.

Of special interest in spiropyran molecules is the length of the C<sub>spiro</sub>–O bond in the pyran ring (C2–O1 in the structures



**Figure 3**  
Inter- and intramolecular hydrogen bonds in (I) [symmetry code: (i)  $-x + 1, -y + 2, -z$ ].

the same as in the mother compound (SP1), whereas in (II) this bond is noticeably shorter, close to the shortest interatomic distance observed for 2-oxindane spiropyran (Bulanov *et al.*, 2009). Thus it can be proposed that functionalization of the mother spiropyran (SP1) with chelatore groups in the case of benzocarbohydrazone (II) can suppress its photochromic properties, while thiosemicarbazone (I) is not expected to perform worse than SP1.

In crystals of (I), centrosymmetrically bound complementary pairs of molecules are formed by two equivalent intermolecular hydrogen bonds, *viz.* N2–H2N...S1<sup>i</sup> and S1...H2N<sup>i</sup>–N2<sup>i</sup> [symmetry code: (i)  $-x + 1, -y + 2, -z$ ]. Thus, an eight-membered ring involving two donors and two acceptors is observed (see Fig. 3 and Table 2). In the same dimers, short intermolecular contacts, *viz.* C9–H9...S1<sup>i</sup> and S1...H9<sup>i</sup>–C9<sup>i</sup>, are also observed.

In the crystal structure of (II), a molecule of solvent (acetone) interacts with the hydrazone molecule by an intermolecular hydrogen bond (N2–H2N...O1S), a short contact (C27–H27...O1S, 0.30 Å less than the van der Waals sum) and a C–H... $\pi$  interaction of the C3S–H3SC group with the aromatic system (C3A/C4'–C7'/C7A) of the oxindane moiety [H3SC...centroid distance = 2.68 Å, C3S...centroid = 3.634 (3) Å and C3S–H3SC...centroid = 165°]. The acetone solvent molecule is also linked with another hydrazone molecule by a strong C–H...O hydrogen bond (C3S–H3SB...O3<sup>ii</sup>; see Table 3 for details). Between hydrazone molecules, C–H... $\pi$  interactions with near to optimal characteristics are observed between the C7'–H7' group and the C22–C27 ring at ( $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ) [H7'...centroid distance = 2.80 Å, C7'...centroid = 3.715 (3) Å and C7'–H7'...centroid = 163°].

reported here), which is involved in the opening–closing of the pyran ring reaction. For comparison, some geometric parameters of SP1, taken from Bulanov *et al.* (2009), are presented in Table 1. It can be seen that in (I) the C2–O1 bond is nearly

## Experimental

Hydrazones (I) and (II) were obtained using similar procedures. To a solution of SP1 (0.01 M) in ethanol, a hot ethanol solution (0.01 M) of

the corresponding hydrazide was added. A precipitate started to appear after 15 min of reflux. The solution was cooled to room temperature and left for 1 h. The precipitated crystalline solid [red in the case of (I) and yellow in the case of (II)] was filtered off and washed twice with hot petroleum ether. The yield was 52% for (I) and 60% for (II), and the melting point was 463 K for (I) and 436 K for (II). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of its solution in benzene. In the case of (II), a mixed benzene–acetone (1:1 *v/v*) solution was employed for crystal growth.

## Compound (I)

### Crystal data

$C_{27}H_{25}N_3O_3S$	$\gamma = 77.714 (4)^\circ$
$M_r = 471.56$	$V = 1176.1 (3) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.4023 (14) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.4893 (15) \text{ \AA}$	$\mu = 0.17 \text{ mm}^{-1}$
$c = 15.210 (3) \text{ \AA}$	$T = 120 \text{ K}$
$\alpha = 87.020 (4)^\circ$	$0.45 \times 0.30 \times 0.25 \text{ mm}$
$\beta = 83.192 (4)^\circ$	

### Data collection

Bruker SMART 1000 CCD area-detector diffractometer	9676 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2005)	4139 independent reflections
$T_{\min} = 0.941$ , $T_{\max} = 0.958$	2089 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.075$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$	307 parameters
$wR(F^2) = 0.139$	H-atom parameters constrained
$S = 1.15$	$\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$
4139 reflections	$\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$

## Compound (II)

### Crystal data

$C_{27}H_{24}N_2O_4 \cdot C_3H_6O$	$V = 2602.6 (12) \text{ \AA}^3$
$M_r = 498.56$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.591 (2) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 17.272 (5) \text{ \AA}$	$T = 100 \text{ K}$
$c = 17.569 (5) \text{ \AA}$	$0.60 \times 0.40 \times 0.20 \text{ mm}$
$\beta = 93.265 (5)^\circ$	

### Data collection

Bruker APEXII CCD area-detector diffractometer	20745 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2005)	4568 independent reflections
$T_{\min} = 0.959$ , $T_{\max} = 0.983$	2752 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.092$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	339 parameters
$wR(F^2) = 0.096$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
4568 reflections	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

The H atoms of the NH and OH groups were found in difference Fourier maps, but were subsequently constrained to ride on their parent atoms, with N–H and O–H distances of 0.90 and 0.85 Å, respectively, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N,O})$ . All other H atoms were

**Table 1**

Selected geometric parameters (Å, °) for (I), (II) and SP1.

	(I)	(II)	SP1 <sup>a</sup>
O1–C2	1.456 (4)	1.449 (3)	1.4558 (10)
O2'–C2	1.428 (5)	1.429 (3)	1.4185 (11)
O1–C8A	1.377 (4)	1.370 (3)	1.3570 (10)
O2'–C1'	1.471 (4)	1.464 (3)	1.4614 (11)
C3–C2	1.488 (5)	1.495 (4)	1.4993 (12)
C2–C3A	1.496 (5)	1.503 (3)	1.5044 (12)
N1–C9	1.288 (5)	1.286 (3)	
O1–C2–C3	111.3 (3)	111.6 (2)	112.44 (7)
C8A–O1–C2	119.4 (3)	119.13 (19)	120.54 (7)
C2–O2'–C1'	111.0 (3)	111.43 (17)	112.06 (7)

Reference: (a) Bulanov *et al.* (2009).

**Table 2**

Hydrogen-bond geometry (Å, °) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N3–H3N $\cdots$ N1	0.90	2.27	2.668 (5)	107
O2–H2 $\cdots$ N1	0.85	1.94	2.646 (4)	140
N2–H2N $\cdots$ S1 <sup>i</sup>	0.90	2.46	3.341 (4)	165
C9–H9 $\cdots$ S1 <sup>i</sup>	0.95	2.81	3.660 (4)	150

Symmetry code: (i)  $-x + 1, -y + 2, -z$ .

**Table 3**

Hydrogen-bond geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2–H2N $\cdots$ O1S	0.90	2.11	3.000 (3)	169
O2–H2 $\cdots$ N1	0.85	1.84	2.591 (3)	147
C27–H27 $\cdots$ O1S	0.95	2.42	3.351 (3)	167
C3S–H3SB $\cdots$ O3 <sup>ii</sup>	0.98	2.45	3.323 (3)	148

Symmetry code: (ii)  $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ .

placed in geometrically optimized positions and constrained to ride on their parent atoms, with C–H = 0.95 (aromatic), 0.99 (methylene) or 0.98 Å (methyl), and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic and methylene groups, and  $1.5U_{\text{eq}}(\text{C})$  for methyl groups.

To improve the refinement results, several reflections [one in the case of (I) and seven in the case of (II)] with too high values of  $\delta(F^2)/\text{e.s.d.}$  and with  $F_o^2 < F_c^2$  were deleted from the refinement.

Data collection: SMART (Bruker, 1998) for (I); APEX2 (Bruker, 2005) for (II). Cell refinement: SAINT-Plus (Bruker, 1998) for (I); SAINT (Bruker, 2005) for (II). Data reduction: SAINT-Plus for (I); SAINT for (II). For both compounds, program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: Mercury (Macrae *et al.*, 2006); 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: LG3049). Services for accessing these data are described at the back of the journal.

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