

Thermolysis of Some Spirobenzopyran-3',2-[1,3,4]oxadithiino[5,6-*c*]benzopyran-4'-ones in the Presence of Some Homodienes and Crystallographic Studies of Some Adducts

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The very reactive α -oxo-thioketone derivatives **2a–d**, generated *via* thermolysis of spirobenzopyran-3',2-[1,3,4]oxadithiino[5,6-*c*]benzopyran-4'-ones **1a–d**, reacted with 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene under [4+2]-cycloaddition to afford spirobenzopyran-3',6-thiapyran-4'-one adducts **3a–d** and spirobenzopyran-3',3-thiabicyclo[2.2.2]oct-5-en-4'-one adducts **4a–d**, respectively. On the other hand, the reaction of α -oxo-thioketones **2a–d** with isoprene afforded regioselectively only 3-methyl-thiapyran derivatives **5a–d**. Single crystal X-ray diffraction studies of **4b**, **4c**, and **5a** give a good support for the established structure.

Key words: α -Oxo-thioketones, Spirobenzopyran-3',6-thiapyran-4'-one, Hetero-Diels-Alder Reaction

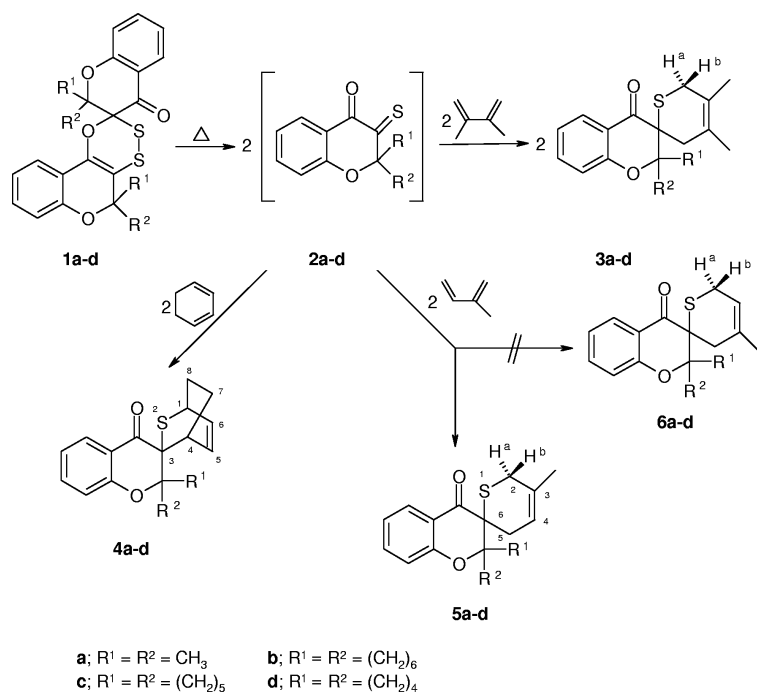
Some α -oxo-thioketone compounds are stable and can be isolated in pure state in the monomeric form [1–7]. Previously, it was reported that some chromene-derived- α -oxo-thioketones were isolated as dimers with an 1,3,4-oxadithiin structure *via* the reaction of α -chloro- α -chlorothioketone compounds with tertiary phosphanes or potassium iodide [8–11]. Recently [11], [4+2] cycloaddition reactions of some 3-thioxo-benzopyran-4-ones (generated *in situ* *via* reduction of the corresponding α -chloro-sulfonylchlorides with potassium iodide) with 2,3-dimethyl-1,3-butadiene have been reported. Herein we describe the thermolysis of spirobenzopyran-3',2-[1,3,4]oxadithiino[5,6-*c*]benzopyran-4'-ones in the presence of 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene, and isoprene.

Results and Discussion

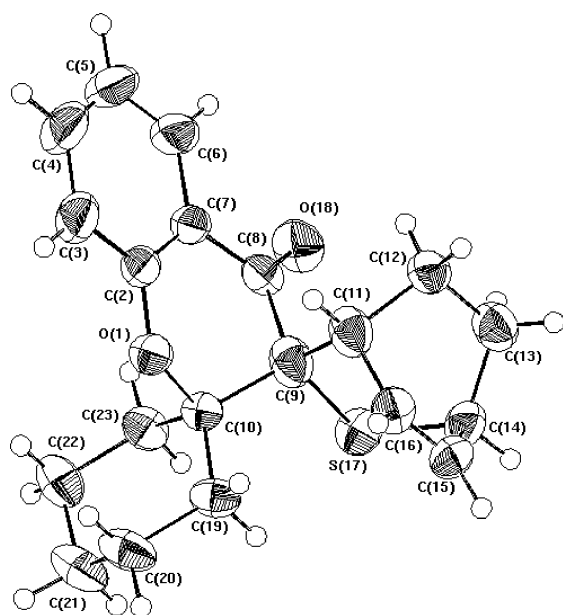
The superdipolarophilic α -oxo-thioketone intermediates **2a–d** were generated *in situ* by thermal cleavage of the spirobenzopyran-3',2-[1,3,4]oxadithiino[5,6-*c*]benzopyran-4'-ones **1a–d** in a retro Diels-Alder reaction in dry benzene and reacted with 2,3-dimethyl-1,3-butadiene to afford the corresponding spirobenzopyran-3',6-thiapyran-4'-one adducts **3a–d** in higher yield than that obtained previously [11]

(Scheme 1). These products were purified by crystallization rather than column chromatography as in the previous study [11]. 3,4-Dimethyl-dispiro[cyclopentane-1'',2'-benzopyran-3',6- Δ^3 -thiapyran]-4'-one (**3d**) was not described before; therefore it was characterized by elemental analysis and spectral data (IR, ¹H and ¹³C NMR, MS). The IR spectrum shows a strong band at $\nu = 1681\text{ cm}^{-1}$ for the carbonyl group. The ¹H NMR spectrum of **3d** shows two doublets at $\delta = 2.72$ and 2.85 ppm ($J = 13.5\text{ Hz}$) corresponding to the 2-CH^aH^b, and the 5-CH₂ protons appeared with the cyclopentane protons. The ¹³C NMR spectrum shows signals for C-5 at $\delta = 28.69$, C-2 at $\delta = 32.45$, C-6 at $\delta = 56.58$, C-2' at $\delta = 83.60$, and C-4' at $\delta = 184.21\text{ ppm}$. The mass spectrum of **3d** shows the prominent ion peak at $m/z = 314$.

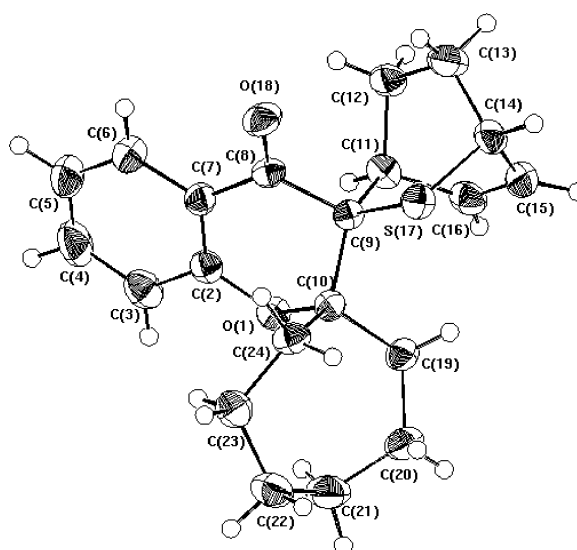
Similarly, α -oxo-thioketone intermediates **2a–d** cyclized with 1,3-cyclohexadiene in dry benzene during 1 h and afforded the corresponding spirobenzopyran-3',3-(2-thiabicyclo[2.2.2]oct-5-ene)-4'-one adducts **4a–d** in very high yields (Scheme 1). The spectral data (IR, ¹H and ¹³C NMR, MS) as well as elemental analyses support the established structures of **4a–d**. The IR spectra of **4a–d** exhibit the carbonyl stretching vibration band at $\nu = 1682\text{--}1695\text{ cm}^{-1}$. The ¹H NMR spectra show 4-CH_{sp3} at $\delta = 3.19\text{--}3.24\text{ ppm}$ as multiplet, 1-CH_{sp3} at $\delta = 3.54\text{--}3.59\text{ ppm}$



Scheme 1.

Fig. 1. Molecular structure of **4b**; ellipsoids of thermal vibration are shown at 50% probability.

as multiplet, 5-CH_{sp2} at $\delta = 6.35-6.37$ as doublet with $J = 7.5$ Hz, and 6-CH_{sp2} at $\delta = 6.49-6.51$ ppm as doublet with $J = 7.5$ Hz. ¹³C NMR spectra of **4a,c** show signals for C-4 at $\delta = 32.76, 32.75$, C-1 at

Fig. 2. Molecular structure of **4c**; ellipsoids of thermal vibration are shown at 50% probability.

$\delta = 35.30, 35.28$, C-3 at $\delta = 66.50, 67.01$, C-2' at $\delta = 85.43, 85.35$, C-4' at $\delta = 193.67, 193.62$ ppm, respectively. The mass spectra of **4a-d** showed the prominent ion peak at 285 (M - H, 100%), 339 (M - H, 40%), 325 (M - H, 42%), 311 (M - H, 45%), respectively. Single crystal X-ray diffraction studies of

Crystal data	Compound		
	4b	4c	5a
Empirical formula	C ₂₁ H ₂₄ O ₂ S	C ₂₀ H ₂₂ O ₂ S	C ₁₆ H ₁₈ O ₂ S
Formula weight	340.485	326.458	274.382
Shape/color	prismatic/colorless	prismatic/colorless	prismatic/colorless
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Temperature [K]	298	298	298
Wavelength [Å]	0.71073	0.71073	0.71073
Unit cell dimensions			
<i>a</i> [Å]	17.8172(4)	16.7972(6)	12.0521(7)
<i>b</i> [Å]	7.3398(2)	7.7481(2)	6.8170(4)
<i>c</i> [Å]	13.7273(3)	13.4379(3)	17.5541(13)
α [°]	90.00	90.00	90.00
β [°]	109.2113(8)	110.2144(8)	100.444(2)
γ [°]	90.00	90.00	90.00
Volume [Å ³]	1695.21(7)	1641.06(8)	1418.30(2)
<i>Z</i>	4	4	4
Density (calculated) [mg m ⁻³]	1.334	1.321	1.285
θ Range for data collection [°]	2.91–27.49	2.91–27.49	2.91–21.49
Index ranges			
<i>h</i>	0 → 23	0 → 21	0 → 12
<i>k</i>	0 → 9	0 → 10	0 → 6
<i>l</i>	–17 → 16	–17 → 16	–18 → 17
Reflections, measured	4176	4008	2998
independent	4141	4014	1737
observed	2430	2487	1156
Data/restraints/parameters	2430/0/217	2487/0/208	1152/0/172
Goodness-of-fit	1.751	0.851	1.827
<i>R</i> Indices (all data), <i>R</i>	0.103	0.061	0.072
<i>wR</i>	0.123	0.074	0.086
<i>R</i> Indices [<i>I</i> ≥ 3σ(<i>I</i>)]	0.047	0.037	0.044
Max./min. electron density [e Å ⁻³]	0.33/–0.34	0.31/–0.21	0.28/–0.33

Table 1. Crystal data and details of structure determination of **4b**, **c**, and **5a**.

4b, **c** (Fig. 1, 2) add a good evidence for the established structures.

On the other hand, α -oxo-thioketone intermediates **2a–d** reacted with isoprene under the same reaction conditions, as described above, to afford in a completely regioselective manner adducts **5a–d** rather than the isomers **6a–d** (Scheme 1). Spectral data (IR, ¹H and ¹³C NMR, MS) and elemental analyses established the structure of **5a–d**. The IR spectra of **5a–d** reveal a strong band at $\nu = 1682$ – 1689 cm⁻¹ assignable to the carbonyl stretching vibration band. The ¹H NMR spectra of **5a–d** show two doublets at $\delta = 2.66$ – 2.69 and 2.86 – 2.87 ppm ($J = 16.5$ – 16.8 Hz) corresponding to the 2-CH^aH^b protons. ¹³C NMR spectra of **5a**, **c** show signals for C-5 at $\delta = 26.51$, 26.63, C-2 at $\delta = 32.76$, 32.73, C-6 at $\delta = 53.30$, 53.38, C-2' at $\delta = 85.43$, 85.51, and C-4' at $\delta = 193.67$, 193.50 ppm, respectively. The mass spectra of **5a–d** show the prominent ion peak at 274 (*M*⁺, 52%), 327 (*M* – H, 100 %), 313 (*M* – H, 100 %), 299

(*M* – H, 100 %), respectively. The structure of **5a** was confirmed by a single crystal X-ray diffraction study (Fig. 3).

Crystal structures of **4b**, **4c** and **5a**

The molecular graphics of compounds **4b** and **4c** together with the chosen numbering scheme are shown in Figs. 1 and 2, some selected bond lengths, bond angles, and torsion angles are given in Table 2. Selected hydrogen bonds are summarized in Tables 3 and 4.

Referring to the numbering scheme shown in Figs. 1 and 2, it is shown that the two compounds have the same basic units, which consists of a benzopyrane ring, spiro-connected to a thiabicyclo[2.2.2]octane system; they differ only in the attachment at the position C10, with a cyclohexane ring in the first compound and cycloheptane ring in the other one. The pyran-4-one ring in the two compounds takes the half-chair shape;

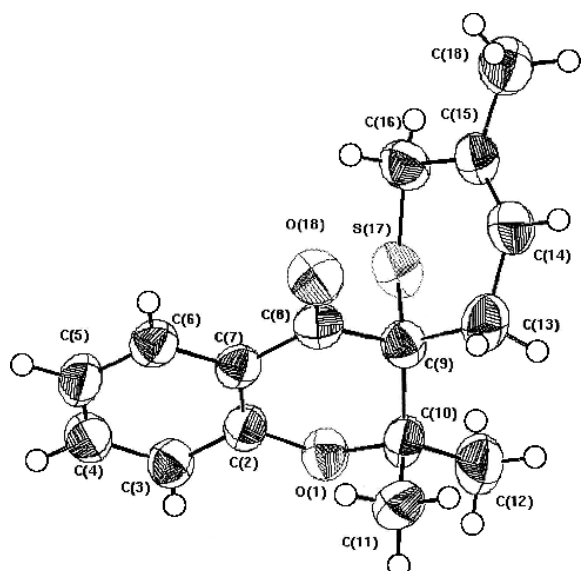


Fig. 3. Molecular structure of **5a**; ellipsoids of thermal vibration are shown at 50% probability.

hereby, the deviation of atom C9 from the best plane passing through this ring is 0.699(2) Å in compound **4b** and $-0.658(2)$ Å in compound **4c**. All the bond lengths and bond angles are within the normal range [16]. From the values of bond lengths and bond angles given in Table 2 it is clear that C10 exists in sp^3 hybridization. The dihedral angle between the planes defined by S17, C11, C9, C14 and C12, C13, C15, C16 is equal to $90.62(4)^\circ$ and $90.03(4)^\circ$ in the two compounds, which means that the plane containing the sulfur atom is perpendicular to the other plane. The cyclohexane ring in **4b** takes the chair conformation, as confirmed by the deviation of atoms C10 and C21 from the best plane passing through C19, C20, C22 and C23 (for C10: 0.595(2) Å; for C21: $-0.068(3)$ Å). The cycloheptane ring in **4c** seems to have a two-fold rotation axis passing through C10 and bisecting the bond C21-C22. Finally, the crystal structures of the two compounds are stabilized by hydrogen bonding as shown in Tables 3 and 4.

The structure of compound **5a** is shown in Fig. 3. Here a benzopyran-4-one ring is spiro-connected with a thiapyrane ring. The calculation of the best plane of the pyran ring shows the planarity of the atoms C8-C7-C2-O1-C10 with a deviation of atom C9 from this plane of 0.591(4) Å indicating the half-chair conformation. The same behavior is observed for the thiapyrane ring, where the sulfur atom deviates from the best plane of C9-C13-C14-C15-C16 by $-0.836(1)$ Å.

Table 2. Selected bond lengths, bond angles, and torsion angles (Å, °) for **4b**, **c**.

Atom	4b	4c
O1-C2	1.358(2)	1.364(2)
C7-C2	1.392(3)	1.391(2)
C9-C8	1.538(2)	1.546(2)
C9-C10	1.567(2)	1.566(2)
C10-O1	1.468(2)	1.475(2)
C9-C11	1.576(2)	1.583(2)
C11-C12	1.547(3)	1.549(2)
C12-C13	1.536(3)	1.541(2)
C13-C14	1.527(3)	1.528(2)
C14-C15	1.490(3)	1.489(2)
C15-C16	1.320(3)	1.318(2)
C16-C11	1.505(3)	1.507(2)
C14-S17	1.839(2)	1.845(2)
S17-C9	1.822(2)	1.826(1)
C10-C19	1.525(2)	1.533(2)
C10-C24		1.544(2)
C10-O1-C2	118.07(14)	117.55(10)
O1-C2-C7	122.8(2)	122.63(13)
C7-C8-C9	114.29(14)	115.02(12)
C8-C9-C10	106.18(14)	107.11(11)
C9-C10-O1	108.69(12)	107.87(11)
C9-C10-C19	114.95(15)	113.47(11)
C9-C10-C23	109.34(13)	
C9-C10-C24		109.09(11)
C9-C11-C12	109.99(13)	110.51(12)
C11-C12-C13	111.0(2)	110.24(13)
C12-C13-C14	109.6(2)	110.13(13)
C13-C14-C15	108.7(2)	109.10(14)
C14-C15-C16	115.1(2)	115.37(14)
C15-C16-C11	115.7(2)	115.56(14)
C14-S17-C9	97.69(8)	97.59(7)
O1-C10-C24		109.9(11)
C14-S17-C9-C11	2.29(12)	3.74(12)
C14-S17-C9-C10	$-129.06(13)$	130.22(13)
C14-S17-C9-C8	113.64(13)	$-112.24(13)$
C9-S17-C14-C13	$-61.30(14)$	60.25(14)
C9-S17-C14-C15	57.50(14)	$-58.55(14)$
C2-O1-C10-C9	47.00(15)	$-50.9(2)$
C2-O1-C10-C23	$-72.2(2)$	
C2-O1-C10-C24		67.9(2)
C10-O1-C2-C7	$-13.5(2)$	18.8(2)
C2-O1-C10-C19	169.5(2)	$-171.3(2)$
C10-O1-C2-C3	167.2(2)	$-162.1(2)$

Table 3. Hydrogen-bonding geometry of compound **4b**.

D-H...A	D-H	H...A	D...A	D-H...A
C16-H16 ^v ...O18	0.960(2)	2.480(1)	3.347(2)	150.15(5)

Symmetry codes: ^v $x, -1/2 - y, z - 1/2$.

Some selected bond lengths, bond angles, and torsion angles, are given in Table 5. The intramolecular distances of the molecule are consistent with those published for similar compounds [17]. It is worth mentioning that the bond lengths $C9-S17 = 1.836(3)$ Å and $S17-C16 = 1.796(3)$ Å reflect the divalency of the sulfur atom. Finally, networks of intermolecular forces

Table 4. Hydrogen-bonding geometry of compound **4c**.

D-H...A	D-H	H...A	D...A	D-H...A
C16-H16 ^v ...O18	0.960(2)	2.481(1)	3.381(2)	156.18(8)

Symmetry codes: ^v $x, 1/2 - y, 1/2 + z$.Table 5. Selected bond lengths, bond angles, and torsion angles for **5a**.

S17–C9	1.836 (3)	S17–C16	1.796 (3)
O1–C10	1.475 (3)	O1–C2	1.366 (3)
O18–C8	1.220 (3)	C7–C2	1.390 (4)
C7–C8	1.479 (4)	C10–C9	1.549 (4)
C10–C11	1.508 (4)	C10–C12	1.509 (4)
C9–C13	1.534 (4)	C9–C8	1.525 (4)
C14–C15	1.310 (4)	C14–C13	1.501 (4)
C15–C16	1.491 (4)	C15–C18	1.507 (4)
C9–S17–C16	99.58 (13)	C10–O1–C2	117.9 (2)
O1–C10–C9	108.3 (2)	O1–C10–C11	108.1 (2)
O1–C10–C12	102.4 (2)	C9–C10–C11	111.3 (2)
C14–C15–C16	122.7 (3)	C14–C15–C18	123.0 (3)
C16–C15–C18	114.3 (3)	C9–C13–C14	117.6 (2)
C16–S17–C9–C10	–177.0 (3)	C9–S17–C16–C15	47.6 (3)
C16–S17–C9–C13	–53.0 (3)	C16–S17–C9–C8	66.6 (3)
C10–O1–C2–C7	19.7 (4)	C2–O1–C10–C9	–49.9 (3)
C2–O1–C10–C11	70.9 (4)	C10–O1–C2–C3	–161.2 (5)
C2–O1–C10–C12	–171.3 (4)	C6–C7–C2–O1	–178.6 (6)

Table 6. Hydrogen-bonding geometry of compound **5a**.

D-H...A	D-H	H...A	D...A	D-H...A
C12 H 12A ^{vi} ...C18	0.960(3)	3.036(3)	3.922(4)	132.06(6)
C18-H18A ^{vii} ...O18	0.960(3)	2.719(2)	3.319(4)	121.20(4)

Symmetry codes: ^{vi} $2 - x, -y, 1 - z$; ^{vii} $2 - x, y - 1/2, 3/2 - z$.

stabilize the structure of compound **5a** as shown in Table 6.

Experimental Section

Melting points were determined in an open glass capillary using an Electrothermal IA 9000 SERIES digital melting point apparatus (Electrothermal, Essex, U.K.) and are uncorrected. Microanalyses were performed on Elementar-Vario EL, Microanalytical Unit, Central Services Laboratory, National Research Centre, Cairo, Egypt. The NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer. ¹H spectra were run at 300 MHz and ¹³C NMR spectra were run at 75.46 MHz in CDCl₃ as a solvent. Chemical shifts are quoted in δ and were related to that of the solvents (Cairo University, Faculty of Science). Splitting patterns were designed as follow: s = singlet; d = doublet; m = multiplet. Mass spectra were recorded on Shimadzu GCMS-QP 1000EX (EI, 70 eV) spectrometers. IR spectra were obtained with a Bruker-Vectro 22 instrument for KBr wafers (Microanalytical Center of Cairo University). Compounds **1a**, **d** [9], **1b** [11], **1c** [10] were prepared according to literature procedures. Yields of the products were reported after recrystallization.

Spirobenzopyran-3',6- Δ^3 -thiapyran-4'-one **3**; general procedure

A mixture of **1** (3 mmol) and 2,3-dimethyl-1,3-butadiene (0.7 mL, 6 mmol) in dry benzene (20 mL) was boiled under reflux for 1 h. The reaction mixture was evaporated under reduced pressure to dryness. The residue was treated with 5 mL of ethanol to give the solid products **3**.

2',2',3,4-Tetramethyl-spirobenzopyran-3',6- Δ^3 -thiapyran-4'-one (**3a**)

From **1a**, crystallization from ethanol, colorless crystals, yield 1.4 g (80%) (lit. [11]: 64%). – M.p. 99–101 °C (lit. [11]: 99–101 °C).

3,4-Dimethyl-dispiro[cycloheptane-1'',2'-benzopyran-3',6- Δ^3 -thiapyran]-4'-one (**3b**)

From **1b**, crystallization from ethanol, colorless crystals, yield 1.0 g (75%) (lit. [11]: 40%). – M.p. 84–87 °C (lit. [11]: 84–87 °C).

3,4-Dimethyl-dispiro[cyclohexane-1'',2'-benzopyran-3',6- Δ^3 -thiapyran]-4'-one (**3c**)

From **1c**, crystallization from ethanol, colorless crystals, yield 1.9 g (97%) (lit. [11]: 85%). – M.p. 109–112 °C (lit. [11]: 110–113 °C).

3,4-Dimethyl-dispiro[cyclopentane-1'',2'-benzopyran-3',6- Δ^3 -thiapyran]-4'-one (**3d**)

From **1d**, crystallization from ethanol, colorless crystals, yield 1.5 g (85%). – M.p. 90–93 °C. – IR: ν = 1681 cm^{–1} (C=O). – ¹H NMR: δ = 1.73–2.58 (m, 16 H, 4 CH₂+5-CH₂+2 CH₃), 2.72 (d, J = 13.5 Hz, 1 H, 2-CH^aH^b), 2.85 (d, J = 13.5 Hz, 1 H, 2-CH^aH^b), 6.89–7.05 (m, 2 H, Ar-H), 7.45 (d, J = 8.1 Hz, 1 H, Ar-H), 7.87 (d, J = 8.1 Hz, 1 H, Ar-H). – ¹³C NMR: δ = 19.18 (4-CH₃), 19.89 (3-CH₃), 24.71, 25.22 (C-3'' and C-4''), 28.69 (C-5), 32.45 (C-2), 34.30, 35.53 (C-2'' and C-5''), 56.58 (C-6), 83.60 (C-2'), 113.95 (C-4), 116.90 (C-3), 117.80 (C-8'), 121.41 (C-6'), 124.43 (C-4a'), 127.00 (C-5'), 135.83 (C-7'), 161.82 (C-8a'), 184.21 (C-4'). – MS: m/z (%) = 314 (100) [M], 300 (15), 281 (20), 194 (15), 121 (70). – C₁₉H₂₂O₂S (314.43): calcd. C 72.57, H 7.05, S 10.19; found C 72.45, H 6.98, S 10.02.

Spirobenzopyran-3',3-(2-thiabicyclo[2.2.2]oct-5-ene)-4'-one (**4**)

A mixture of **1** (3 mmol) and 1,3-cyclohexadiene (0.6 mL, 6 mmol) in dry benzene (20 mL) was boiled under reflux for 1 h. The reaction mixture was evaporated under reduced

pressure to dryness. The residue was treated with 5 mL of ethanol to give the solid products **4**.

2',2'-Dimethyl-spirobenzopyran-3',3-(2-thiabi-cyclo[2.2.2]oct-5-ene)-4'-one (4a)

From **1a**, crystallization from ethanol, colorless crystals, yield 1.4 g (85%). – M. p. 132–135 °C. – IR: $\nu = 1687\text{ cm}^{-1}$ (C=O). – ^1H NMR: $\delta = 1.14$ (s, 3 H, CH₃), 1.54 (s, 3 H, CH₃), 1.59–1.65 (m, 2 H, 7-CH₂), 2.18–2.20 (m, 2 H, 8-CH₂), 3.19–3.21 (m, 1 H, 4-CH), 3.54–3.57 (m, 1 H, 1-CH), 6.37 (t, $J = 7.2$ Hz, 1 H, 5-CH), 6.49 (t, $J = 7.2$ Hz, 1 H, 6-CH), 6.90 (d, $J = 8.1$ Hz, 1 H, Ar-H), 6.98 (t, $J = 7.8$ Hz, 1 H, Ar-H), 7.43–7.49 (m, 1 H, Ar-H), 7.88 (dd, $J = 7.8, 1.2$ Hz, 1 H, Ar-H). – ^{13}C NMR: $\delta = 22.60$ (2'-CH₃), 22.85 (C-7), 26.17 (2'-CH₃), 26.51 (C-8), 32.76 (C-4), 35.30 (C-1), 66.50 (C-3), 85.43 (C-2'), 117.90 (C-5), 120.28 (C-6), 120.85 (C-8'), 127.59 (C-6'), 133.42 (C-4a'), 133.70 (C-5'), 135.72 (C-7'), 157.68 (C-8a'), 193.67 (C-4'). – MS: m/z (%) = 286 (78) [M], 285 (100) [M–H], 270 (7), 205 (15), 192 (19), 172 (26), 165 (23), 137 (49), 120 (54), 91 (36), 85 (58), 77 (53). – C₁₇H₁₈O₂S (286.37): calcd. C 71.29, H 6.33, S 11.19; found C 71.03, H 6.20, S 10.99.

Dispiro[cycloheptane-1'',2'-benzopyran-3',3-(2-thiabi-cyclo[2.2.2]oct-5-ene)]-4'-one (4b)

From **1b**, crystallization from ethanol, colorless crystals, yield 1.3 g (96%). – M. p. 173–175 °C. – IR: $\nu = 1695\text{ cm}^{-1}$ (C=O). – ^1H NMR: $\delta = 0.95$ –1.90 (m, 16 H, cycloheptane-H + 7-CH₂ + 8-CH₂), 3.20–3.22 (m, 1 H, 4-CH), 3.54–3.58 (m, 1 H, 1-CH), 6.36 (t, $J = 7.5$ Hz, 1 H, 5-CH), 6.49 (t, $J = 7.5$ Hz, 1 H, 6-CH), 6.98–7.03 (m, 2 H, Ar-H), 7.46–7.52 (m, 1 H, Ar-H), 7.90 (dd, $J = 7.5, 1.5$ Hz, 1 H, Ar-H). – MS: m/z (%) = 340 (31) [M], 339 (40) [M–H], 259 (14), 226 (20), 214 (25), 192 (13), 177 (24), 125 (23), 121 (71), 90 (84), 79 (100). – C₂₁H₂₄O₂S (340.46): calcd. C 74.07, H 7.10, S 9.41; found C 73.80, H 6.97, S 9.07.

Dispiro[cyclohexane-1'',2'-benzopyran-3',3-(2-thiabi-cyclo[2.2.2]oct-5-ene)]-4'-one (4c)

From **1c**, crystallization from ethanol, colorless crystals, yield 1.8 g (95%). – M. p. 200–202 °C. – IR: $\nu = 1682\text{ cm}^{-1}$ (C=O). – ^1H NMR: $\delta = 0.95$ –2.01 (m, 14 H, cyclohexane-H + 7-CH₂ + 8-CH₂), 3.21–3.24 (m, 1 H, 4-CH), 3.54–3.59 (m, 1 H, 1-CH), 6.36 (t, $J = 7.5$ Hz, 1 H, 5-CH), 6.49 (t, $J = 7.5$ Hz, 1 H, 6-CH), 6.98–7.03 (m, 2 H, Ar-H), 7.46–7.51 (m, 1 H, Ar-H), 7.90 (dd, $J = 7.5, 1.5$ Hz, 1 H, Ar-H). – ^{13}C NMR: $\delta = 21.61, 21.83, 22.85, 25.15, 26.53, 27.80, 31.87$ (cyclohexane-C + C-7 + C-8), 32.75 (C-4), 35.28 (C-1), 67.01 (C-3), 85.35 (C-2'), 117.51 (C-5), 120.29 (C-6), 120.91 (C-8'), 127.58 (C-6'), 133.42 (C-4a'), 133.71 (C-5'), 135.70 (C-7'), 157.65 (C-8a'), 193.62 (C-4'). – MS:

m/z (%) = 326 (32) [M], 325 (42) [M–H], 245 (14), 212 (21), 200 (25), 173 (21), 126 (29), 121 (70), 115 (19), 97 (30), 92 (60), 79 (100). – C₂₀H₂₂O₂S (326.44): calcd. C 73.58, H 6.79, S 9.82; found C 73.39, H 6.68, S 9.72.

Dispiro[cyclopentane-1'',2'-benzopyran-3',3-(2-thiabi-cyclo[2.2.2]oct-5-ene)]-4'-one (4d)

From **1d**, crystallization from ethanol, colorless crystals, yield 1.7 g (93%). – M. p. 193–196 °C. – IR: $\nu = 1693\text{ cm}^{-1}$ (C=O). – ^1H NMR: $\delta = 1.69$ –2.59 (m, 12 H, cyclopentane-H + 7-CH₂ + 8-CH₂), 3.21–3.24 (m, 1 H, 4-CH), 3.54–3.58 (m, 1 H, 1-CH), 6.35 (t, $J = 7.5$ Hz, 1 H, 5-CH), 6.51 (t, $J = 7.5$ Hz, 1 H, 6-CH), 6.98–7.02 (m, 2 H, Ar-H), 7.47–7.51 (m, 1 H, Ar-H), 7.89 (dd, $J = 7.5, 1.5$ Hz, 1 H, Ar-H). – MS: m/z (%) = 312 (28) [M], 311 (45) [M–H], 231 (20), 198 (20), 173 (30), 126 (29), 121 (65), 115 (15), 97 (21), 79 (100). – C₁₉H₂₀O₂S (312.41): calcd. C 73.04, H 6.45, S 10.26; found C 72.85, H 6.39, S 10.06.

3-Methyl-spiro(benzopyran-3',6- Δ^3 -thiapyran)-4'-one (5)

A mixture of **1** (3 mmol) and isoprene (0.6 mL, 6 mmol) in dry benzene (20 mL) was refluxed for 1 h. The reaction mixture was evaporated under reduced pressure to dryness. The residue was treated with 5 mL of ethanol to give the solid products **5**.

2',2',3-Trimethyl-spiro(benzopyran-3',6- Δ^3 -thiapyran)-4'-one (5a)

From **1a**, crystallization from ethanol, colorless crystals, yield 1.4 g (88%). – M. p. 124–126 °C. – IR: $\nu = 1689\text{ cm}^{-1}$ (C=O). – ^1H NMR: $\delta = 1.35$ (s, 3 H, CH₃), 1.65 (s, 3 H, CH₃), 1.77 (s, 3 H, CH₃), 2.24–2.46 (m, 2 H, 5-CH₂), 2.66 (d, $J = 16.5$ Hz, 1 H, 2-CH^aH^b), 2.86 (d, $J = 16.5$ Hz, 1 H, 2-CH^aH^b), 5.82 (s, 1 H, 4-CH), 6.87 (d, $J = 8.1$ Hz, 1 H, Ar-H), 6.96–7.01 (m, 1 H, Ar-H), 7.41–7.46 (m, 1 H, Ar-H), 7.88–7.92 (m, 1 H, Ar-H). – ^{13}C NMR: $\delta = 22.60$ (CH₃), 22.85 (CH₃), 26.17 (CH₃), 26.51 (CH₂), 32.76 (CH₂), 53.30 (C-6), 85.43 (C-2'), 117.50 (C-4), 120.28 (C-3), 120.85 (C-8'), 121.51 (C-6'), 127.59 (C-4a'), 133.42 (C-5'), 135.72 (C-7'), 157.68 (C-8a'), 193.67 (C-4'). – MS: m/z (%) = 274 (78) [M], 273 (26) [M–H], 259 (79), 241 (15), 161 (25), 154 (28), 147 (11), 139 (47), 121 (100), 112 (30), 91 (28), 86 (31), 77 (31). – C₁₆H₁₈O₂S (274.36): calcd. C 70.03, H 6.61, S 11.68; found C 69.78, H 6.57, S 11.39.

3-Methyl-dispiro(cycloheptane-1'',2'-benzopyran-3',6- Δ^3 -thiapyran)-4'-one (5b)

From **1b**, crystallization from ethanol, colorless crystals, yield 1.0 g (77%). – M. p. 106–109 °C. – IR: $\nu = 1682\text{ cm}^{-1}$ (C=O). – ^1H NMR: $\delta = 1.17$ –2.40 (m, 17 H, cycloheptane-H + 5-CH₂ + CH₃), 2.69 (d, $J = 16.8$ Hz, 1 H,

2-CH^aH^b), 2.87 (d, $J = 16.8$ Hz, 1 H, 2-CH^aH^b), 6.36 (t, $J = 7.5$ Hz, 1 H, 5-CH), 5.61 (s, 1 H, 4-CH), 6.96–7.06 (m, 2 H, Ar-H), 7.45–7.51 (m, 1 H, Ar-H), 7.91–7.94 (m, 1 H, Ar-H). – MS: m/z (%) = 328 (80) [M], 327 (100) [M–H], 294 (76), 284 (33), 270 (15), 224 (18), 215 (13), 200 (25), 193 (21), 160 (25), 147 (12), 120 (73), 111 (76), 93 (35), 77 (40). – C₂₀H₂₄O₂S (328.45): calcd. C 73.13, H 7.36, S 9.76; found C 72.85, H 7.28, S 9.53.

3-Methyl-dispiro(cyclohexane-1'',2'-benzopyran-3',6-Δ³-thiapyran)-4'-one (5c)

From **1c**, crystallization from ethanol, colorless crystals, yield 1.6 g (90%). – M. p. 109–112 °C. – IR: $\nu = 1687$ cm^{−1} (C=O). – ¹H NMR: $\delta = 1.19$ –2.39 (m, 15 H, cyclohexane-H + 5-CH₂ + CH₃), 2.66 (d, $J = 16.8$ Hz, 1 H, 2-CH^aH^b), 2.86 (d, $J = 16.8$ Hz, 1 H, 2-CH^aH^b), 5.62 (s, 1 H, 4-CH), 6.96–7.04 (m, 2 H, Ar-H), 7.44–7.50 (m, 1 H, Ar-H), 7.91–7.93 (m, 1 H, Ar-H). – ¹³C NMR: $\delta = 21.63$, 21.82, 22.87, 25.15, 26.17, 26.55, 26.63, 32.73 (cyclohexane-C + 2-CH₂ + 5-CH₂ + CH₃), 53.38 (C-6), 85.51 (C-2'), 117.50 (C-4), 120.30 (C-3), 120.85 (C-8'), 121.53 (C-6'), 127.60 (C-4a'), 133.42 (C-5'), 135.70 (C-7'), 157.68 (C-8a'), 193.50 (C-4'). – MS: m/z (%) = 314 (82) [M], 313 (100) [M–H], 280 (75), 270 (35), 256 (15), 210 (14), 200 (22), 193 (23), 160 (26), 147 (13), 120 (72), 111 (75), 93 (36), 77 (36). – C₁₉H₂₂O₂S (314.43): calcd. C 72.57, H 7.05, S 10.19; found C 72.29, H 6.96, S 9.89.

3-Methyl-dispiro(cyclopentane-1'',2'-benzopyran-3',6-Δ³-thiapyran)-4'-one (5d)

From **1d**, crystallization from ethanol, colorless crystals, yield 1.5 g (85%). – M. p. 115–117 °C. – IR: $\nu = 1685$ cm^{−1}

(C=O). – ¹H NMR: $\delta = 1.55$ –2.60 (m, 13 H, cyclopentane-H + 5-CH₂ + CH₃), 2.67 (d, $J = 16.8$ Hz, 1 H, 2-CH^aH^b), 2.86 (d, $J = 16.8$ Hz, 1 H, 2-CH^aH^b), 5.61 (s, 1 H, 4-CH), 6.91–7.01 (m, 2 H, Ar-H), 7.44–7.50 (m, 1 H, Ar-H), 7.90–7.93 (m, 1 H, Ar-H). – MS: m/z (%) = 300 (20) [M], 299 (100), 266 (80), 256 (25), 242 (19), 200 (40), 193 (36), 121 (70), 77 (37). – C₁₈H₂₀O₂S (300.40): calcd. C 71.96, H 6.71, S 10.67; found C 71.63, H 6.69, S 10.50.

X-ray data collection

X-ray crystallographic data were collected on an Enraf-Nonius 590 Kappa CCD single crystal diffractometer with graphit-monochromatized MoK α radiation ($\lambda = 0.71073$ Å). The intensities were collected at room temperature using φ - ω scan mode; the crystal to detector distance was 40 mm. Further details are summarized in Table 1. The cell refinement and data reduction were carried out using Denzo and Scalepak programs [12], the crystal structures were solved by the Direct Method using the SIR92 program [13] which revealed the positions of all non-hydrogen atoms, and refined by a full-matrix least-squares refinement based on F^2 using the maXus package [14]. The temperature factors of all non-hydrogen atoms were refined anisotropically, then hydrogen atoms were introduced as a riding model with C–H = 0.960 Å and refined isotropically. The molecular graphics were prepared using the ORTEP program [15].

CCDC-608128 (**4b**), -608129 (**4c**) and -608130 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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