Dyes and Pigments 84 (2009) 19–24

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

7-Nitro- and 7-aminosubstituted spiropyrans of 1-benzothieno[3,2-*b*]pyrrole

Valerii Z. Shirinian [a,*], Alexey A. Shimkin [a], Arthur K. Mailian [a], Dmitry V. Tsyganov [a], Leonid D. Popov [b], Mikhail M. Krayushkin [a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp., 47, 119991 Moscow, Russian Federation*
[b] *Southern Federal University, 344104, Rostov-on-Don, str. B. Sadovaya 105, Russian Federation*

ARTICLE INFO

Article history:
Received 5 May 2009
Received in revised form
16 June 2009
Accepted 18 June 2009
Available online 27 June 2009

Keywords:
Spiropyrans
Benzothienopyrroles
Bi-functional compounds
Salicylideneanilines
Dithienylethenes

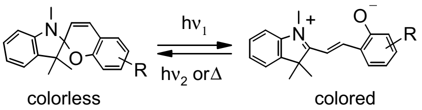
ABSTRACT

Amino and nitro derivatives of spiropyrans based on 1-benzothieno[3,2-*b*]pyrrole were synthesized employing an efficient method for the reduction of nitro group in thienopyrroles and spiropyrans. Novel bi-functional compounds, containing salicylideneaniline and dithienylethene fragments, along with spiropyran were prepared from the aminospiropyran derivative.

1. Introduction

The design and synthesis of organic photochromic compounds is an intense research area because of their potential applications for optoelectronic devices, including photoswitching materials and optical storage elements [1–4], that make the development of synthetic methods of photochromic compounds and the investigation of influence of their structure on spectral, physical and applied properties urgently needed.

One of promising classes of photochromic organic dyes are spiropyran derivatives which undergo photo-transformation under UV-light irradiation leading to formation of metastable merocyanine dyes. The most known photochromic spiropyrans belong to indole derivatives.



Recently, we have developed an efficient method for the synthesis of photochromic spiro compounds [5,6] and merocyanine dyes [7] based on close analogues of indole – thienopyrroles, and studied their spectral properties [8,9]. In this work, we present the synthesis of nitro-substituted spiropyrans of benzothienopyrrole series and the development of regioselective method for the reduction of nitro- to amino group in spiropyran and thienopyrroline systems. Early unknown hybrid photochromic compounds are synthesized by the reaction of aminospiropyran with salicylic aldehydes or dithienylmaleic anhydride.

2. Results and discussion

For the preparation of nitrospiropyrans **5a–c** early described method of synthesis of thienopyrrolinespiropyrans was used [10,11]. As starting material benzothienone **1** was utilized (Scheme 1). The only difference of this synthesis is the using of ethyl acetate as solvent in hydrazone hydrochloride preparation stage because of very low solubility of hydrazone **2** in benzene.

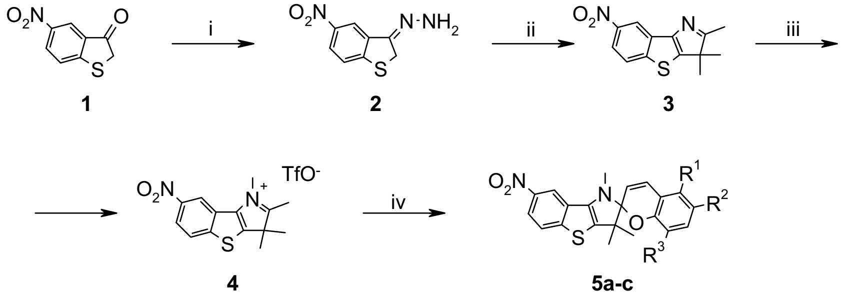
When in this reaction 3,5-dinitrosalicylic aldehyde was used the open form of spiropyran, the merocyanine **5d** was isolated that is in agreement with published data [12] (Scheme 2). The ^{1}H NMR spectrum of this compound showed signals of the CMe_2 group as a singlet, thus confirming the existence of a non-cyclic structure.

Aminospiropyrans have attracted much attention not only for the elucidation of the influence of amino group on the photo- and thermochromic properties but also as potential intermediates for the preparation of various derivatives. To prepare aminospiropyrans, two synthetic routes were explored; firstly, the nitro group in thienopyrrolenine **3** was reduced and subsequent

---

* Corresponding author. fax: +7 495 1376939.
E-mail address: shir@ioc.ac.ru (V.Z. Shirinian).

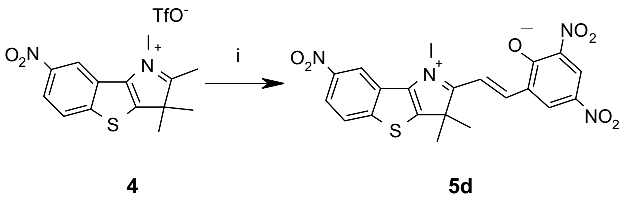
0143-7208/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2009.06.007



5a, $R^1 = R^3 = H$, $R^2 = NO_2$; **5b**, R^1, $R^2 = (CH)_4$,
$R^3 = H$; **5c**, $R^1 = R^2 = H$, $R^3 = OMe$

i, $NH_2NH_2{*}H_2O$, EtOH; ii, 1. HCl_g, EtOAc; 2. $CH_3C(O)CH(CH_3)_2$, C_6H_6;
iii, MeOTf, CH_3CN; iv, aldehyde, piperidine, EtOH

Scheme 1.



i, 2-hydroxy-3.5-dinitrobenzaldehyde,
piperidine, EtOH

Scheme 2.

alkylation enabled the preparation of the spiropyran derivative (Scheme 3, route **A**). The second route involved the synthesis of nitrospiropyran **5b** followed by reduction (Route **B**).

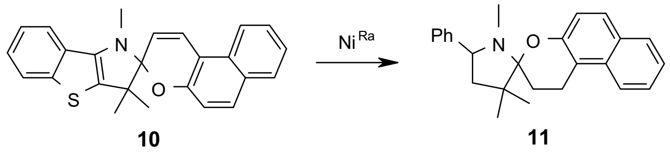
7-Amino-3*H*-benzothienopyrrole **6** was synthesised using various reducing agents (tin dichloride in methanolic solution of hydrochloric acid, zinc dust in acetic acid, sodium hydrosulfide in ethanol); optimum results were achieved using an excess of NaHS in boiling EtOH. Benzothienopyrrole **6** was found to be labile and decomposed at room temperature, partially being oxidized by atmospheric oxygen to the starting compound **3**.

However, attempts to prepare the methylated salt **7** by methylation of the aminobenzothienopyrrole **6** with methyltriflate or methyl iodide in acetonitrile under an argon atmosphere failed, insofar as it produce an inseparable complex mixture. Obviously, the reaction proceeds non-regioselectively and leads to the mixture of products with different degrees of alkylation.

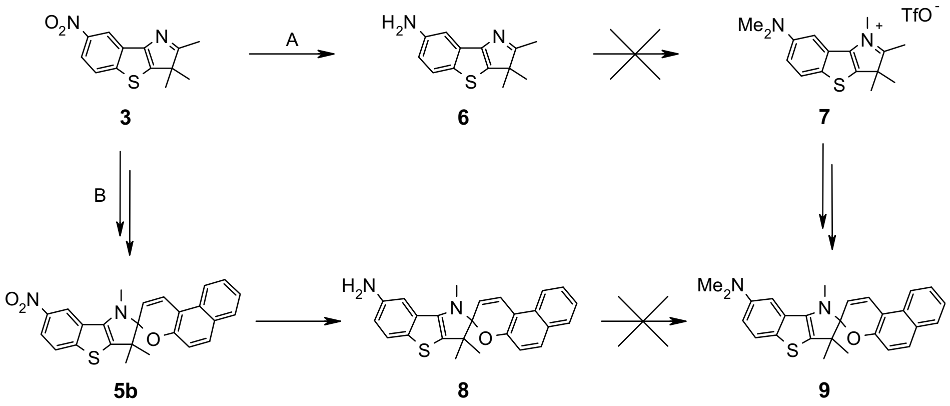
This convinced us to use route **B** (Scheme 3). However, there is no published literature concerning the reduction of the nitro group in the indole part of photochromic spiropyrans although, two methods for the reduction of nitro group in the pyran fragment of spiropyran have been reported using hydrogen [13] or hydrazine hydrate [14] on Raney nickel, and tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$) [15] in acidic medium.

The first method is not acceptable for benzothienopyrrole derivatives since the thiophene ring is too sensitive to Raney nickel, and the desulfurization of thiophene ring occurs. Actually, we have found that the reaction of compound **10** with Raney nickel under mild conditions leads to desulfurized and reduced spiro compound **11** (Scheme 4). Therefore, Raney nickel could not be applied for the reduction of thienopyrrole derivatives.

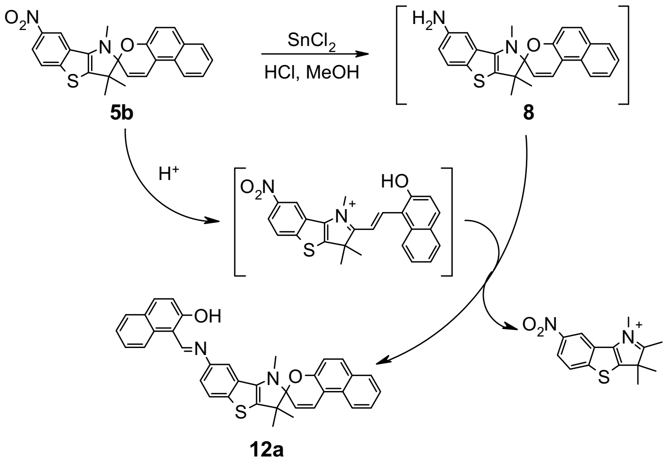
When nitrospiropyran **5b** was treated with tin (II) chloride dihydrate, unexpected results were obtained: azomethine **12a** instead of aminospiropyran **8** was isolated. The structure of compound **12a** was proved both by spectral methods and independent synthesis. Apparently, the mechanism of the hybrid



Scheme 4.



Scheme 3.



Scheme 5.

compound **12** formation includes Michael-type reaction of amine **8** with second spiropyran molecule activated by acid with subsequent elimination of thienopyrrolium salt (Scheme 5).

To test this proposed reaction pathway we have carried out the reaction of spiropyran **10** with aniline, and the expected product **13** has actually been isolated (Scheme 6). It is significant that in the literature there is no similar substitution of methylene base in spiropyran molecule by another nucleophiles.

To exclude the formation of azomethine **12a** the reduction reaction of compound **5b** was carried out by sodium hydrosulfide under basic conditions, and the target aminospiropyran **8** was obtained in good yield (Scheme 7).

The attempt of alkylation of aminospiropyran **8** with methyl triflate or methyl iodide led to inseparable salt-like products instead of dimethylamino derivative **9** (Scheme 3).

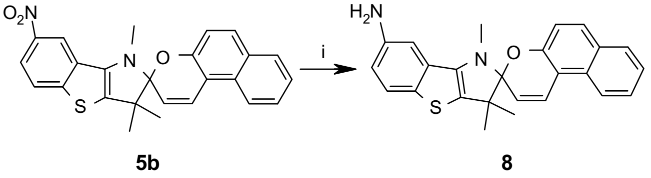
To synthesize the hybrid photochromic compounds bearing spiropyran and salicylideneaniline fragments the aminospiropyran **8** was condensed with different salicylic aldehydes (Scheme 8). The reaction proceeds in the mixture of ethanol and acetic acid, and the Schiff's bases **12a**–**d** were obtained in 35–64% yields.

The formation of diimine **12d** was already observed at room temperature, and therefore the monocondensation product couldn't be obtained.

Compound **15** containing the spiropyran and dithienylethene fragments has been prepared by the reaction of aminospiropyran **8** with dithienylmaleic anhydride **14** under basic conditions. The anion of compound **8** generated in the first stage by lithium hexamethyldisilazide reacts with maleic anhydride **14** giving the hybrid product **15** in 57% yield (Scheme 9).

The prepared compounds **12a**–**d** and **15** contain two and more functional groups, and they are of interest for the design of novel smart materials for optoelectronic application since the salicylidenaniline [16], diarylethene [17], and spiropyran [1] fragments are potential photochromic systems.

In summary, early unknown nitrospiropyrans of 1-benzothieno[3,2-*b*]pyrrole series have been synthesized. An efficient method for the reduction of nitro group in thienopyrrole and spiropyran systems has been developed. Novel bi-functional compounds, containing salicylideneaniline and dithienylethene fragments, along with spiropyran system, have been prepared starting from aminospiropyran derivative.



5b **8**

i, NaSH, EtOH

Scheme 7.

3. Experimental

3.1. General

^{1}H and ^{13}C NMR spectra were performed on Bruker AM-300 or WM-250 spectrometers. Mass spectra were obtained on a Kratos mass spectrometer (70 eV) with direct sample injection into the ion source. Melting points were measured on a Boetius hot stage and were not corrected. Column chromatography was performed using silica gel 60 (70–230 mesh), TLC analysis was conducted on silica gel 60 F_{254} plates. Commercially available (Acros, Merck) reagents and solvents were used. Chromatography products were purchased from Merck. 5-Nitro-1-benzothiophen-3(2H)-one **1** [18], spiropyran **10** [10] and anhydride **14** [19] were prepared by known procedures.

3.2. Synthesis of starting compounds

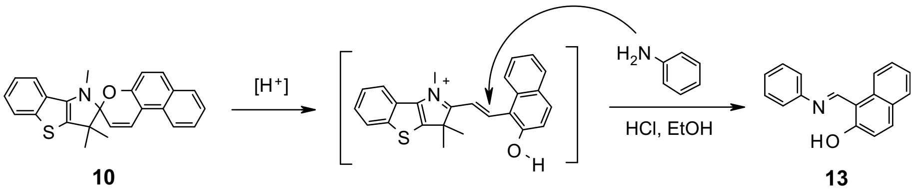
3.2.1. 5-Nitro-1-benzo[b]thiophen-3(2H)-one hydrazone **2**

p-Toluenesulfonic acid (0.86 g, 5 mmol) and hydrazine hydrate (15 mL, 0.3 mol) were added to a stirred solution of benzothiophen-3-one **1** (9.75 g, 0.05 mol) in ethanol (15 mL). The solution immediately became dark. The mixture was refluxed for 5 h, maintained for 10–12 h at room temperature, and the ensuing precipitate was filtered off and dried in air.

Yellow powder; yield 79%; mp. dec. 160–163 °C (ethanol); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 4.13$ (s, 2H, CH_2), 6.88 (br. s, 2H, NH_2), 7.52 (d, $J = 8.6$ Hz, 1H, H^{arom}), 8.00 (dd, $J = 2.4$, 8.6 Hz, 1H, H^{arom}), 8.08 (d, $J = 2.4$ Hz, 1H, H^{arom}). MS: m/z (%) = 209 (100) $[M]^+$, 192 (88) $[M - NH_3]^+$. Anal. Calcd. (%) for $C_8H_7N_3O_2S$: C, 45.92; H, 3.37; N, 20.08. Found: C, 46.17; H, 3.71; N, 19.70.

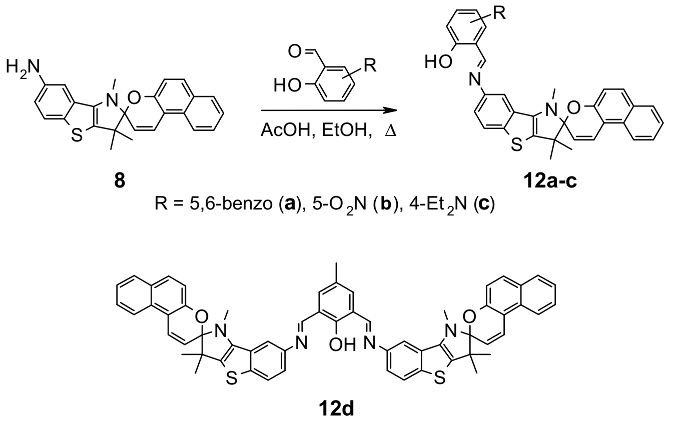
3.2.2. 2,3,3-Trimethyl-7-nitro-3H-[1]benzothieno[3,2-b]pyrrole **3**

Hydrogen chloride gas was passed through a cooled to 0 °C solution of 5-nitro-1-benzo[*b*]thiophen-3(2*H*)-one hydrazone **2** (2.0 g, 12 mmol) in ethyl acetate (15 mL) with stirring. The solution darkened, and a solid precipitated. The precipitate was filtered off,



10 **13**

Scheme 6.



Scheme 8.

washed with cooled ethyl acetate, and dried in air to yield 2.2 g of hydrazone **2** hydrochloride as pale yellow solid. The product was used on the next stage without additional purification. 3-Methylbutan-2-one (ed. Note: flammable; irritant) (1.54 mL, 14 mmol) was added to a suspension of hydrochloride of benzothiophen-3-one hydrazone (2.2 g, 11 mmol) in anhydrous benzene (30 mL). The reaction mixture was refluxed for 2 h during which the precipitate dissolved. The reaction mixture was cooled, poured into 200 mL of water and extracted with ethyl acetate (3 × 50 mL). The organic fractions were combined, washed with water, and concentrated under reduced pressure. After solvent evaporation, the residue was purified by chromatography on silica gel using a 3:1 petroleum ether/ethyl acetate mixture as the eluent.

Brown powder; yield 64%. mp. 122–124 °C (ethanol). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.45$ (s, 6H, CMe_2), 2.37 (s, 3H, CH_3), 7.91 (d, 1H, $J = 8.8$ Hz, H^{arom}), 8.15 (d, 1H, $J = 8.8$ Hz, H^{arom}), 8.94 (s, 1H, H^{arom}). MS: m/z (%) = 260 (100) $[M]^+$, 245 (22) $[M\text{–}Me]^+$, 219 (80) $[M\text{–}MeCN]^+$. Anal. Calcd. (%) for $C_{13}H_{12}N_2O_2S$: C, 59.98; H, 4.65; N, 10.76. Found: C, 59.80; H, 4.83; N, 10.66.

3.3. *Preparation of spiropyrans **5a–d** (total procedure)*

To a solution of 3*H*-benzothienopyrrole **3** (0.26 g, 1 mmol) in absolute acetonitrile (5 mL) methyl trifluoromethanesulfonate (methyltriflate; ed note: Flammable liquid and vapour; moisture sensitive; severe irritant; incompatible materials with strong acids, strong oxidants, bases) (0.12 mL, 1.1 mmol) was added. The reaction mixture was refluxed for 1.5 h and cooled. After evaporation of solvent absolute ethanol (5 mL), corresponding *o*-hydroxyaldehyde (1.0 mmol) and piperidine (0.1 mL, 1.0 mmol) were added to the residue, and the reaction mixture was refluxed for 3–12 h. Completion of the reaction was monitored by TLC (eluent petrol. ether/ethyl acetate 5:1). The products were purified by column chromatography or recrystallization.

3.3.1. *1,3,3-Trimethyl-6′,7-dinitrospiro[2,3-dihydro-1H-[1]benzothieno[3,2-b]pyrrole-2,2′-2H-chromene] **5a***

Orange powder; yield 74%; mp. 231–232 °C (petrol. ether/benzene). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.30$ (s, 3H, ½CMe_2), 1.36 (s, 3H, ½CMe_2), 3.11 (s, 3H, NCH_3), 5.95 (d, $J = 10.5$ Hz, 1H, CH), 6.86 (d, $J = 8.5$ Hz, 1H, H^{arom}), 6.98 (d, $J = 10.5$ Hz, 1H, CH), 7.89 (d, $J = 8.5$ Hz, 1H, H^{arom}), 8.02–8.15 (m, 3H, H^{arom}), 8.67 (d, $J = 2.0$ Hz, 1H, H^{arom}). MS: m/z (%) = 423 (90) $[M]^+$, 408 (100) $[M\text{–}Me]^+$. Anal. Calcd. (%) for $C_{21}H_{17}N_3O_5S$: C, 59.57; H, 4.05; N, 9.92. Found: C, 59.37; H, 4.42; N, 9.74.

3.3.2. *1,3,3-Trimethyl-7-nitrospiro[2,3-dihydro-1H-[1]benzothieno[3,2-b]pyrrole-2,3′-3H-benzo[f]chromene] **5b***

Red powder; yield 53%; mp. 204–205 °C (petrol. ether). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.34$ (s, 3H, ½CMe_2), 1.42 (s, 3H, ½CMe_2), 3.12 (s, 3H, NMe), 5.89 (d, $J = 10.5$ Hz, 1H, CH), 7.06 (d, $J = 9.2$ Hz, 1H, H^{arom}), 7.37 (t, $J = 7.9$ Hz, 1H, H^{arom}), 7.55 (t, $J = 7.9$ Hz, 1H, H^{arom}), 7.61–7.72 (m, 2H, H^{arom}), 7.76 (d, $J = 8.5$ Hz, 1H, H^{arom}), 7.87 (d, $J = 9.2$ Hz, 1H, H^{arom}), 8.03–8.13 (m, 2H, H^{arom}), 8.70 (d, $J = 2.0$ Hz, 1H, H^{arom}). MS: m/z (%) = 428 (100) $[M]^+$, 413 (99) $[M - CH_3]^+$, 398 (99) $[M\text{–}2CH_3]^+$, 383 (78) $[M - 3\ CH_3]^+$. Anal. Calcd. (%) for $C_{25}H_{20}N_2O_3S$: C, 70.07; H, 4.70; N, 6.54. Found: C, 70.12; H, 4.81; N, 6.69.

3.3.3. *1,3,3-Trimethyl-8′-methoxy-7-nitrospiro[2,3-dihydro-1H-[1]benzothieno[3,2-b]pyrrole-2,2′-2H-chromene] **5c***

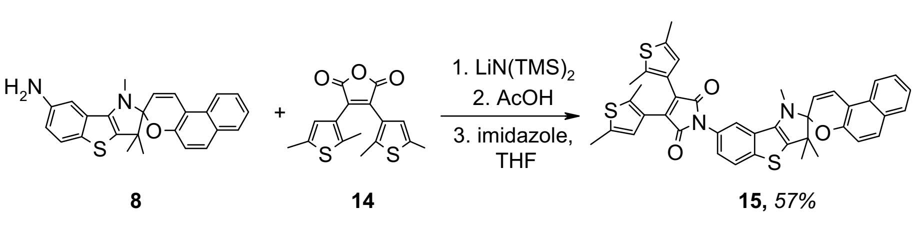
Red powder; yield 71%; mp. 223–225 °C (petrol. ether/benzene). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.27$ (s, 3H, ½CMe_2), 1.39 (s, 3H, ½CMe_2), 3.11 (s, 3H, NMe), 3.73 (s, 3H, OMe), 5.77 (d, $J = 10.5$ Hz, 1H, CH), 6.69–6.75 (M, 1H, H^{arom}), 6.77–6.83 (M, 2H, H^{arom}), 6.86 (d, $J = 10.5$ Hz, 1H, CH), 7.85 (d, $J = 8.5$ Hz, 1H, H^{arom}), 8.07 (dd, $J = 2.0$, 8.5 Hz, 1H, H^{arom}), 8.66 (d, $J = 2.0$ Hz, 1H, H^{arom}). MS: m/z (%) = 408 (100) $[M]^+$, 393 (50) $[M\text{–}Me]^+$. Anal. Calcd. (%) for $C_{22}H_{20}N_2O_4S$: C, 64.69; H, 4.94; N, 6.86. Found: C, 64.41; H, 4.75; N, 6.87.

3.3.4. *2,4-Dinitro-6-[2-(1,3,3-trimethyl-7-nitro-1,3-dihydro-2H-[1]benzothieno[3,2-b]pyrrol-2-yliden)ethyliden]-2,4-cyclohexadien-1-one **5d***

Dark purple powder; yield 78%; mp. > 350 °C (ethanol). ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 1.92$ (s, 6H, CMe_2), 4.35 (s, 3H, NMe), 8.02–8.71 (m, 5H, H^{arom}), 8.89 (s, 1H, H^{arom}), 9.00 (s, 1H, H^{arom}). MS: m/z (%) = 468 (25) $[M]^+$, 453 (42) $[M\text{–}Me]^+$, 274 (38), 259 (100). Anal. Calcd. (%) for $C_{21}H_{16}N_4O_7S$: calc. C, 53.84; H, 3.44; N, 11.96. Found: C, 53.34; H, 3.50; N, 11.70.

3.4. *Synthesis of 7-amino-2,3,3-trimethyl-3H-[1]benzothieno[3,2-b]pyrrole **6***

A suspension of 7-nitro-3*H*-benzothienopyrrole **3** (0.26 g, 1 mmol) and sodium hydrosulfide (purity 70%, 0.8 g, 10 mmol) in ethanol (10 mL) was refluxed for 3 h. The reaction mixture was cooled, poured into water (100 mL), and extracted with ethyl acetate (3 × 20 mL). The extract was filtered through thin layer of silica gel, and the solvent was evaporated. Yellow viscous oil; yield



Scheme 9.

78%; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.39$ (s, 6H, CMe_2), 2.31 (s, 3H, Me), 3.77 (br. s, 2H, NH_2), 6.72 (dd, 1H, $J = 2.2, 8.6$ Hz, H^{arom}), 7.34 (d, $J = 2.2$ Hz, 1H, H^{arom}), 7.55 (d, $J = 8.6$ Hz, 1H, H^{arom}). MS: m/z (%) = 230 (100) $[M]^+$, 215 (30) $[M–Me]^+$, 189 (27) $[M–MeCN]^+$. Anal. Calcd. (%) for $C_{13}H_{14}N_2S$: C, 67.79; H, 6.13; N, 12.16. Found: C, 66.98; H, 6.05; N, 12.32.

3.5. *The reduction of nitrospiropyran **5b***

A. To a suspension of nitrospiropyran **5b** (0.3 g, 0.7 mmol) and $SnCl_2 \cdot 2H_2O$ (1.1 g, 4.9 mmol) in absolute methanol (15 mL) concentrated hydrochloric acid (0.5 mL) was added. The reaction mixture was refluxed for 5 h, cooled, poured into water (100 mL), and to this mixture 5% solution of KOH in water (100 mL) was added. The obtained blue suspension was extracted with ethyl acetate (3 × 50 mL), and combined organic layers were washed with water. Solvent evaporation gave yellow residue that was purified by column chromatography (eluent petrol. ether/ethyl acetate 4:1), and 0.106 g of 7-{[(2-hydroxy-1-naphthyl)methyliden]amino}-1,3,3-trimethylspiro[2,3-dihydro-1H-[1]benzothieno[3,2-*b*]pyrrole-2,3′-3H-benzo[*f*]chromene] **12a** was obtained.

Yellow powder; yield 55%; mp. 189–191 °C (ethanol). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.35$ (s, 3H, ½CMe_2), 1.42 (s, 3H, ½CMe_2), 3.12 (s, 3H, NMe), 5.92 (d, $J = 10.6$ Hz, 1H, CH), 7.06–7.16 (m, 2H, H^{arom}), 7.29–7.40 (m, 3H, H^{arom}), 7.48–7.58 (m, 2H, H^{arom}), 7.64 (d, $J = 10.6$ Hz, 1H, CH), 7.69 (d, $J = 8.8$ Hz, 1H, H^{arom}), 7.71–7.79 (m, 3H, H^{arom}), 7.82 (d, $J = 9.2$ Hz, 1H, H^{arom}), 7.86 (d, $J = 8.4$ Hz, 1H, H^{arom}), 8.06 (d, $J = 8.8$ Hz, 1H, H^{arom}), 8.12 (d, $J = 8.4$ Hz, 1H, H^{arom}), 9.41 (s, 1H, CH), 15.65 (br. s, 1H, OH). IR (KBr): ν $(cm^{-1}) = 3410$ (OH), 2960, 1624, 1464. MS: m/z (%) = 552 (100) $[M]^+$, 537 (59) $[M–Me]^+$, 394 (83), 169 (42). Anal. Calcd. (%) for $C_{36}H_{28}N_2O_2S \cdot ½H_2O$: C, 76.98; H, 5.20; N, 4.99. Found: C, 76.87; H, 5.50; N, 5.02.

B. A suspension of nitrospiropyran **5b** (1.0 g, 2.3 mmol) and sodium hydrosulfide (purity 70%, 1.9 g, 23 mmol) in ethanol (50 mL) was refluxed for 3 h. The reaction mixture was cooled, poured into water (200 mL), and extracted with ethyl acetate (3 × 20 mL). The extract was washed with water, filtered through thin layer of silica gel, and the solvent was evaporated. After purification by column chromatography (eluent petrol. ether/ethyl acetate 2:1) 0.59 g of 7-amino-1,3,3-trimethylspiro[2,3-dihydro-1*H*-[1]benzothieno[3,2-*b*]pyrrole-2,3′-3*H*-benzo[*f*]chromene] **8** was obtained.

Light green powder; yield 63%; mp. 93–95 °C (petrol. ether). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.31$ (s, 3H, ½CMe_2), 1.38 (s, 3H, ½CMe_2), 3.02 (s, 3H, NMe), 3.65 (br. s, 2H, NH_2), 5.89 (d, $J = 10.5$ Hz, 1H, CH), 6.68 (dd, $J = 2.0$, 8.5 Hz, 1H, H^{arom}), 7.04–7.16 (m, 2H, H^{arom}), 7.35 (t, $J = 7.9$ Hz, 1H, H^{arom}), 7.47–7.63 (m, 3H, H^{arom}), 7.67 (d, $J = 8.9$ Hz, 1H), 7.76 (d, $J = 7.9$ Hz, 1H, H^{arom}), 8.06 (d, $J = 8.5$ Hz, 1H, H^{arom}). IR (KBr): ν $(cm^{-1}) = 3376$, 3452 (NH_2). MS: m/z (%) 398 (36) $[M]^+$, 383 (83) $[M–Me]^+$, 246 (31), 229 (100). Anal. Calcd. (%) for $C_{25}H_{22}N_2OS \cdot 1½H_2O$: C, 70.56; H, 5.92; N, 6.58. Found: C, 70.24; H, 6.11; N, 6.46.

3.6. *Reducing desulfuration of spiropyran **10***

To a suspension of spiropyran **10** (0.2 g, 0.5 mmol) in ethanol (5 mL) a Raney nickel suspension in ethanol (5 mL, 5 fold excess) was added, and the reaction mixture was stirred at room temperature for 16 h. The reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 10 mL). The extract was washed with water and solvent was evaporated. The purification of the residue by column chromatography (eluent: petrol. ether/ethyl acetate – 4:1) gave 40 mg of compound **11**.

Pinkish powder; yield 21%; mp. 118–121 °C (petrol. ether). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.02$ (s, 3H, ½CMe_2), 1.29 (s, 3H, ½CMe_2), 1.56–1.79 (m, 2H, CH_2), 2.27–2.41 (m, 5H, NMe + CH_2), 3.11–3.39 (m, 2H, CH_2), 4.19–4.31 (m, 1H, CH), 7.17 (d, $J = 8.8$ Hz, 1H, H^{arom}), 7.23–7.56 (m, 7H, H^{arom}), 7.68 (d, $J = 8.8$ Hz, 1H, H^{arom}), 7.79 (d, $J = 8.1$ Hz, 1H, H^{arom}), 7.85 (d, $J = 8.8$ Hz, 1H, H^{arom}). MS: m/z (%) 357 (14) $[M]^+$, 201 (100), 186 (56), 156 (47). Anal. Calcd. (%) for $C_{25}H_{27}NO$: C, 83.99; H, 7.61; N, 3.92. Found: C, 83.34; H, 7.40; N, 3.58.

3.7. *The reaction of spiropyran **10** with aniline*

To a solution of spiropyran **10** (50 mg, 0.13 mmol) in ethanol (3 mL) aniline (0.5 mL, 5.5 mmol) and concentrated hydrochloric acid (0.1 mL, 1.0 mmol) were added. The reaction mixture was refluxed for 1 h, cooled, poured into water (50 mL) and extracted with ethyl acetate (3 × 10 mL). The extract was washed with water, and solvent was evaporated. The product **13** was purified by column chromatography (eluent: petrol. ether/ethyl acetate – 10:1).

Yellow crystals; yield 62%; mp. 91–93 °C (lit. 92 °C [20]). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 7.09$ (d, $J = 9.2$ Hz, 1H, H^{arom}), 7.28–7.43 (m, 4H, $3H^{Ph} + H^{arom}$), 7.46 (d, $J = 7.9$ Hz, 2H, H^{Ph}), 7.53 (t, $J = 7.9$ Hz, 1H, H^{arom}), 7.72 (d, $J = 7.9$ Hz, 1H, H^{arom}), 7.81 (d, $J = 9.2$ Hz, 1H, H^{arom}), 8.10 (d, $J = 8.5$ Hz, 1H, H^{arom}), 9.33 (s, 1H, CH = N), 15.49 (br. s, 1H, OH). MS: m/z (%) 247 (18) $[M]^+$, 84 (100).

3.8. *Preparation of azomethines **12a–d***

To a hot solution of aminospiropyran **8** (0.13 g, 0.33 mmol) in abs. ethanol (2 mL) 0.33 mmol (0.16 mmol for compound **12d**) of corresponding *o*-hydroxybenzaldehyde and glacial acetic acid (3 drops) were added. The reaction mixture was refluxed until complete disappearance of starting compounds. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was cooled and the precipitate was filtered off, washed with ethanol and dried in air. The additional amount of product could be isolated from mother waters by column chromatography.

3.8.1. *7-{[(2-Hydroxy-1-naphthyl)methyliden]amino}-1,3,3-trimethylspiro[2,3-dihydro-1H-[1]benzothieno[3,2-b]pyrrole-2,3′-3H-benzo[f]chromene] **12a***

The spectral data for this sample agree with same data for the compound obtained by method *2.5.A*. Yield 64%; mp. 190–193 °C (ethanol).

3.8.2. *7-{[(2-Hydroxy-5-nitrophenyl)methyliden]amino]-1,3,3-trimethylspiro}2,3-dihydro-1H-[1]benzothieno[3,2-b]pyrrole-2,3′-3H-benzo[f]chromene] **12b***

Yellow powder; yield 56%; mp. 247–249 °C (ethanol). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.34$ (s, 3H, ½CMe_2), 1.41 (s, 3H, ½CMe_2), 3.10 (s, 3H, NMe), 5.90 (d, $J = 10.5$ Hz, 1H, CH), 7.04–7.13 (m, 2H, H^{arom}), 7.26 (dd, $J = 2.0$, 8.5 Hz, 1H, H^{arom}), 7.36 (t, $J = 7.9$ Hz, 1H, H^{arom}), 7.54 (t, $J = 7.9$ Hz, 1H, H^{arom}), 7.60–7.79 (m, 4H, H^{arom}), 7.86 (d, $J = 8.5$ Hz, 1H, H^{arom}), 8.06 (d, $J = 8.5$ Hz, 1H, H^{arom}), 8.26 (dd, $J = 2.6$, 9.2 Hz, 1H, H^{arom}), 8.41 (d, $J = 2.6$ Hz, 1H, H^{arom}), 8.77 (s, 1H, CH), 14.57 (s, 1H, OH). IR (KBr): ν $(cm^{-1}) = 3450$ (OH), 2964, 1620, 1336. MS: m/z (%) = 547 (100) $[M]^+$, 532 (63) $[M – Me]^+$, 502 (27), 398 (29). Anal. Calcd. (%) for $C_{32}H_{25}N_3O_4S$: C, 70.18; H, 4.60; N, 7.67. Found: C, 69.43; H, 4.79; N, 7.54.

3.8.3. *7-{[(2-Hydroxy-4-diethylaminophenyl)methyliden]amino}-1,3,3-trimethylspiro[2,3-dihydro-1H-[1]benzothieno[3,2-b]pyrrole-2,3′-3H-benzo[f]chromene] **12c***

Light brown powder; yield 35%; mp. 132–135 °C (ethanol). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.22$ (t, $J = 7.2$ Hz, $CH_2C\underline{H}_3$), 1.32 (s, 3H, ½CMe_2), 1.40 (s, 3H, ½CMe_2), 3.09 (s, 3H, NMe), 3.41 (q, $J = 7.2$ Hz, 2H, $C\underline{H}_2CH_3$), 5.90 (d, $J = 10.5$ Hz, 1H, CH), 6.18–6.30 (m, 2H, H^{arom}), 7.07 (d, J = 8.5 Hz, 1H, H^{arom}), 7.15–7.22 (m, 2H, H^{arom}), 7.35 (t, J = 7.9 Hz, 1H, H^{arom}), 7.54 (t, J = 7.9 Hz, 1H, H^{arom}), 7.58–7.71 (m, 3H, H^{arom}), 7.73–7.80 (m, 2H, H^{arom}), 8.06 (d, J = 8.5 Hz, 1H, H^{arom}), 8.46 (s, 1H, CH). IR (KBr): ν (cm^{-1}) = 3450 (OH), 2968, 1628, 1584, 1520. MS: m/z (%) = 573 (10) $[M]^+$, 558 (19) $[M - Me]^+$, 57 (100). Anal. Calcd. (%) for $C_{36}H_{35}N_3O_2S$: C, 75.36; H, 6.15; N, 7.32. Found C, 74.78; H, 5.99; N, 6.72.

*3.8.4. 2,6-Bis{[(1,3,3-trimethylspiro[2,3-dihydro-1H-[1]benzothieno[3,2-b]pyrrole-2,3′-3H-benzo[f]chromen-7-ylimino)methyl]-4-methylphenol **12d***

Brown powder; yield 46%; mp. 199–202 °C (ethanol). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.33 (s, 6H, ½CMe_2), 1.41 (s, 6H, ½CMe_2), 2.39 (s, 3H, Me), 3.09 (s, 6H, NMe), 5.90 (d, J = 10.5 Hz, 2H, CH), 7.08 (d, J = 8.5 Hz, 2H, H^{arom}), 7.24 (dd, J = 2.0, 8.5 Hz, 2H, H^{arom}), 7.36 (t, J = 7.9 Hz, 2H, H^{arom}), 7.53 (t, J = 7.9 Hz, 2H, H^{arom}), 7.58–7.84 (m, 12H, H^{arom}), 8.06 (d, J = 8.5 Hz, 2H, H^{arom}), 8.91 (br. s, 2H, CH), 14.00 (br. s, 1H, OH). IR (KBr): ν (cm^{-1}) = 3450 (OH), 2960, 1580, 1464. ESI-MS: m/z (%) 925 (100) $[M + H]^+$, 947 (19) $[M + Na]^+$, 1872 (14) $[2M + Na + H]^+$. Anal. Calcd. (%) for $C_{59}H_{48}N_4O_3S_2 \cdot 3H_2O$: C, 72.37; H, 5.56; N, 5.72. Found: C, 72.24; H, 5.60; N, 5.57.

*3.9. Synthesis of 3,4-Bis(2,5-dimethyl-3-thienyl)-1-{1′,3′,3′-trimethyl-1′,3′-dihydrospiro(benzo [f]chromene-3,2′-[1]benzothieno[3,2-b]pyrrol)-7′-yl}-1H-pyrrol-2,5-dione **15***

To a solution of aminospiropyran **8** (51 mg, 0.128 mmol) in abs. tetrahydrofuran (30 mL) 1 M solution of lithium hexamethyldisilazide in tetrahydrofuran (ed. Note: reacts vigorously and exothermally with water, moist air, acids, or alcohols liberating flammable vapors which can ignite; extremely flammable liquid and vapor; may form explosive peroxides. causes severe burns; severely corrosive) (0.4 mL, 0.384 mmol) was added. After stirring the reaction mixture for 15 min a solution of anhydride **14** (41 mg, 0.128 mmol) in THF (8 mL) was added. The reaction mixture was refluxed for 2 h, cooled to room temperature, and glacial acetic acid (2 mL) was added. The mix was refluxed for 1 h, and imidazole (90 mg, 1.28 mmol) was added, and the refluxing was continued for 1 h. After cooling the reaction mixture was poured into 3% solution of hydrochloric acid (70 mL) and extracted with ethyl acetate (3 × 20 mL). The extract was washed with water, and solvent was evaporated. The product **15** was purified by column chromatography (eluent: petrol. ether/ethyl acetate – 15:1).

Yellow powder; yield 57%; mp. 203–205 °C (ethanol). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.33 (s, 3H, ½CMe_2), 1.43 (s, 3H, ½CMe_2), 1.91 (s, 6H, Me), 2.45 (s, 6H, Me), 3.09 (s, 3H, NMe), 5.91 (d, J = 10.5 Hz, 1H, CH), 6.70 (s, 2H, H^{thioph}), 7.00–7.10 (m, 2H, CH + H^{arom}), 7.15–7.34 (m, 2H, H^{arom}), 7.43–7.79 (m, 5H, H^{arom}), 8.05 (d, J = 8.3 Hz, 1H, H^{arom}). MS: m/z (%) = 698 (36) $[M]^+$, 683 (100) $[M–Me]^+$. Anal. Calcd. (%) for $C_{41}H_{34}N_2O_3S_3$: C, 70.46; H, 4.90; N, 4.01. Found: C, 70.79; H, 5.03; N, 3.85.

4. Conclusions

Early unknown nitro-substituted spiropyrans of benzothienopyrrole series have been synthesized. It was shown that the reduction of nitro group in spiropyran system depends strongly on the reaction conditions: the reduction by tin (II) chloride in acidic medium leads to bi-functional compound containing salicylidenaniline group along with spiropyran system, and the using of sodium hydrosulfide under basic conditions results in formation of aminospiropyran, which was utilized for the preparation of different hybrid compounds.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (grant No. 08-03-00865-a).

References

[1] Bertelson RC. Organic photochromic and thermochromic compounds. In: Crano JC, Guglielmetti RJ, editors. Topics in applied Chemistry, vol. 1. , New York: Plenum Press; 1999. p. 11–83.
[2] Minkin VI. Chem Rev 2004;104:2751–76.
[3] Krayushkin MM, Barachevsky VA, Irie M. Heteroatom Chem 2007;18:557–67.
[4] US Pat. 6410754; Chem Abstrs, 1996,125:328510.
[5] Shirinian VZ, Krayushkin MM, Nikalin DM, Shimkin AA, Vorontsova LG, Starikova ZA. Arkivoc 2005;7:72–81.
[6] Krayushkin MM, Shirinian VZ, Nikalin DM. Russ Chem Bull Int Ed 2004;53:720–1.
[7] Shimkin AA, Shirinian VZ, Nikalin DM, Krayushkin MM, Pivina TS, Troitsky NA, et al. Eur J Org Chem 2006:2087–92.
[8] Shirinian VZ, Besugliy SO, Metelitsa AV, Krayushkin MM, Nikalin DM, Minkin VI. J Photochem Photobiol A Chem 2007;189:161–6.
[9] Krayushkin MM, Shirinian VZ, Shimkin AA, Mailian AK, Metelitsa AV, Besugliy SO. J Phys Org Chem 2007;20:845–50.
[10] Shimkin AA, Mailian AK, Shirinian VZ, Krayushkin MM. Synthesis 2007: 2706–10.
[11] Shimkin AA, Shirinian VZ, Mailian AK, Krayushkin MM. Izv. Akad. Nauk, Ser. Khim. Russ Chem Bull, Int Ed, 2009;58(2):376–81.
[12] Zakhs ER, Zvenigorodskaya LA, Leshenyuk NG, Martynova VP. Khim Geterotsikl Soedin 1977:1320–6.
[13] Zhou J, Li Y, Tang Y, Zhao F, Song X, Li E. J Photochem Photobiol A Chem 1995;90:117–23.
[14] Nedoshivin VYu, Zaichenko NL, Glagolev NN, Marevtsev VS. Russ Chem Bull Int Ed 1996;45:1182–4.
[15] Zimmerman T, Brede O. J Heterocycl Chem 2003;40:611–6.
[16] Zgierski MZ, Grabowska A. J Chem Phys 2000;112:6329–37.
[17] Irie M. Chem Rev 2000;100:1685–716.
[18] Dokunikhin NS, Gerasimenko YuE. Zhurn Obsh Khim 1960;30:635–8.
[19] Shirinian VZ, Krayushkin MM, Belen'kii LI, Vorontsova LG, Starikova ZA, Martynkin AYu, et al. Chem Heterocycl Compd 2001;37:77–84.
[20] Knot EB. J Chem Soc 1947:976–8.