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Synthesis of Novel Photochromic Spiro Compounds based on Thieno[3,2-*b*]Pyrroles

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Two routes to thieno[3,2-b]pyrrolenines are developed and new spiropyranes and spirooxazines based on thienopyrrole are synthesized. Benzene ring in the chromene part of the spiro molecule is also replaced with thiophene one to give new merocyanines.

Keywords: merocyanine; spirooxazine; spiropyrane; thieno[3,2-*b*]pyrrole; thieno[3,2-*b*]pyrrolenine

INTRODUCTION

The phenomenon of photochromism of spiropyrans was discovered in the middle of XX century, and the Hirshberg's idea of "photochemical erasable memory" initiated active research on photochromism. Numerous other applications based on reversible changes of color and other physical and chemical properties were suggested – from sunglasses and filters to 3D optical memory and photoswitching of protein activity [1].

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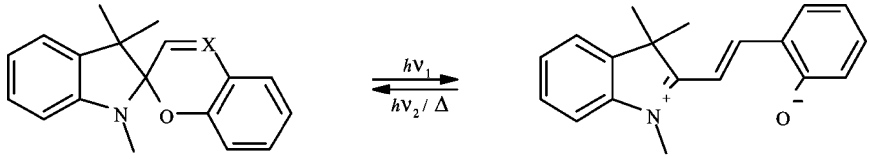
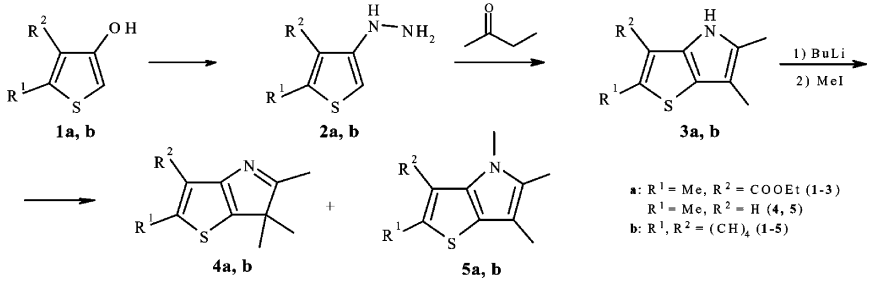


spiro X = CH, N merocyanine

The most of the known spiro compounds are based on indoline. The nearest analog of indole is thieno[3,2-*b*]pyrrole but there are no examples of spiro compounds based on thienopyrrole. In this work we have realized two approaches to the synthesis of thieno[3,2-*b*]pyrrole based spiro-compounds. Also we replaced benzene ring with thiophene one in the chromene part of the spiro molecule. Such a replacement in photochromic system may induce new useful properties and cause the subsequent chemical modification of the products [2,3].

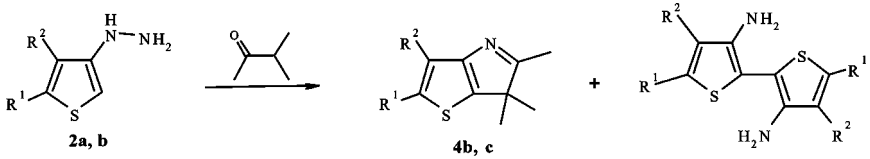
RESULTS AND DISCUSSION

The first synthetic route to thieno[3,2-*b*]pyrrolenines involves the preparation of thienopyrroles followed by alkylation. Thieno[3,2-*b*]pyrroles **3a, b** have been synthesized by the Fischer method starting from 3-hydroxythiophenes **1a, b**. The following step in the preparation of thieno[3,2-*b*]pyrrolenines **4a, b** involves reaction with *n*-butyllithium to form the corresponding salts so we had to remove active COOEt group from the molecule **3a**. Lithium salts of thienopyrroles can react with alkylating agents in two directions, and N-methylthieno[3,2-*b*]pyrroles **5a, b** have been isolated as by-products.



To overcome the limitations of the butyllithium route we have tried to synthesize thieno[3,2-*b*]pyrrolenines directly by Fischer method.

We have studied the reaction of thienylhydrazines **2a, b** with 3-methylbutanone in various conditions.

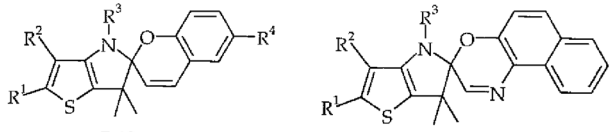


2a, b **4b, c** **6a, b**

R^1 = Me, R^2 = COOEt (**2a, 4c, 6a**); R^1, R^2 = $(CH)_4$ (**2b, 4b, 6b**)

In the most cases we have isolated only the products of benzidine rearrangement **6a, b** [4]. The only conditions that allowed us to obtain thieno[3,2-*b*]pyrrolenines **4b, c** were using of dry hydrogen chloride in benzene [5]. The product precipitates from reaction mixture as salt which is more stable then the free base itself.

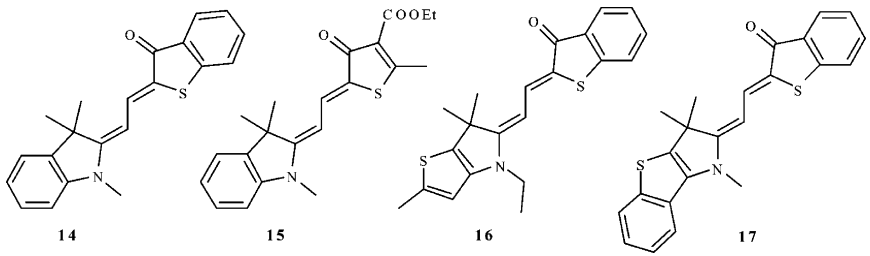
The thienopyrrolenines obtained were alkylated to produce analogs of Fischer's salts, and these salts were used without purification for the synthesis of the corresponding spiropyranes and spirooxazines **7–13** [6].



7-10 **11-13**

7: R^1 = Me, R^2 = H, R^3 = Et, R^4 = H; **8**: R^1 = Me, R^2 = H, R^3 = Et, R^4 = NO_2; **9**: R^1 = Me, R^2 = H, R^3 = Et, R^4 = 4-$MeOC_6H_4$; **10**: R^1, R^2 = $(CH)_4$, R^3 = Me, R^4 = NO_2; **11**: R^1 = Me, R^2 = H, R3 = Et; **12**: R^1 = Me, R^2 = COOEt, R^3 = Et; **13**: R^1, R^2 = $(CH)_4$, R^3 = Me

The next stage of our work was connected to the synthesis of spiro compounds with thiophene ring in the chromene part of molecules. We have prepared the corresponding analogs of salicylic aldehyde on the base of 3-hydroxythiophenes. The spiropyranes obtained (**14–17**) appeared to be in open merocyanine form and had deep color. Perhaps it's because that hydroxythiophenes are more stable in the keto-form than phenols.



14 **15** **16** **17**

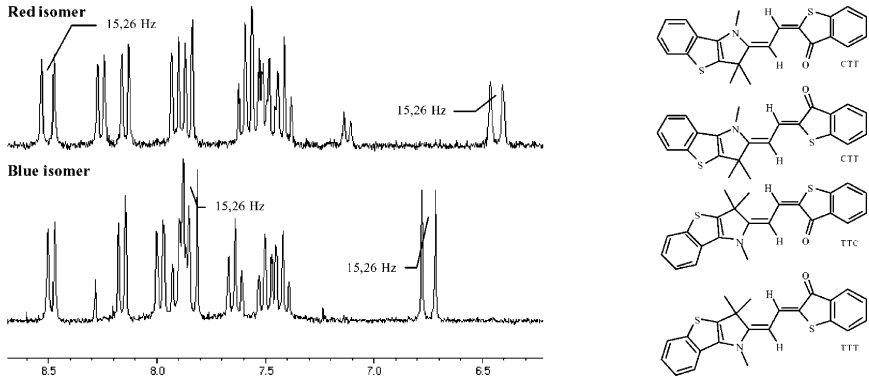


FIGURE 1 ^{1}H NMR spectra of 17 in DMSO-d_6 in the presence of CF_3COOH and four possible isomers.

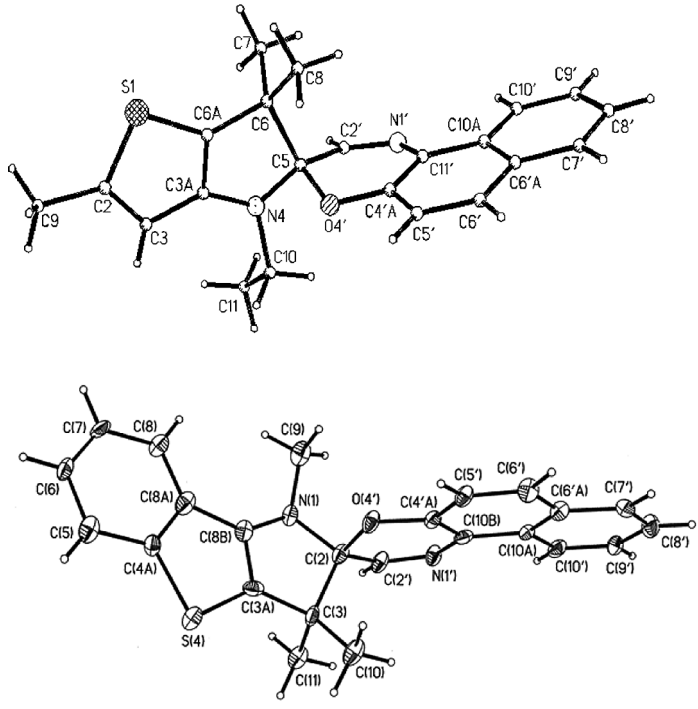


FIGURE 2 Molecular structures of spirooxazines 11 and 13.

We have isolated two forms of the compound **17**: one of them had deep red, the other – deep blue color. Their mass spectra are identical, and NMR spectra are very similar (Fig. 1). The characteristic doublets of the alkenylic protons lie at 6.44 and 8.50 ppm for red and at 6.75 and 7.84 ppm for blue isomer. The large coupling constants (15.26 Hz) indicate that they are mutually trans, so only four structures are possible for these forms.

The structures of all compounds obtained are confirmed by ^{1}H NMR, MASS spectra and elemental analysis. Spirooxazines **11** and **13** were also studied by X-ray diffraction analysis (Fig. 2). Comparing with known spiro[indolino-naphtoxazines] in the molecule **11** the bond $C^{(spiro)}$–N (1.437 Å) is shorter, and the bond $C^{(spiro)}$–O (1.460 Å) is

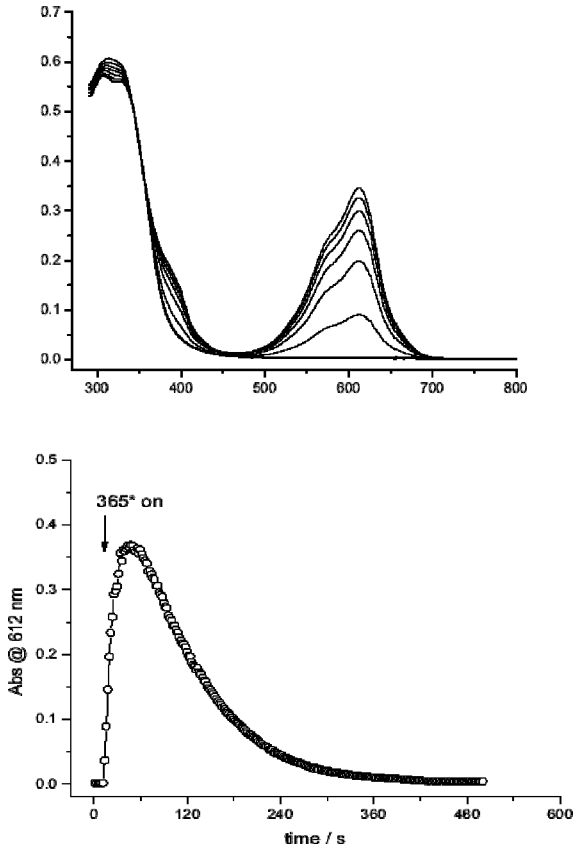


FIGURE 3 Absorption spectra and kinetic plot for the coloration/decoloration process of 8 in toluene.

longer. When thiophene ring is replaced with benzothiophene system the structure becomes similar to indolino-benzoxazines (for the compound **13** $C^{(spiro)}$–N 1.469 Å, $C^{(spiro)}$–O 1.455 Å).

Detailed photochromic studies were carried out for the spiropyran **8**, spirooxazine **11** and merocyanines **14** and **15**. Upon UV irradiation a solution of spiro compound becomes colored, and when the irradiation is stopped, this solution thermally fades to its original state (Fig. 3). The absorption maxima are dependent on solvent: 612 nm in toluene, 565 nm in acetonitrile and 541 nm in ethanol for the spiropyran **8**. Changes in absorption spectra of merocyanines **14, 15** show only *cis–trans* isomerisation but not ring closure process.

CONCLUSION

New convenient methods of the thieno[3,2-*b*]pyrrolenines synthesis have been developed. The first spiropyrans and spirooxazines based on thieno[3,2-*b*]pyrrole have been synthesized. Detailed studies of the compounds obtained have been carried out including photochromic and X-ray analysis. New stable merocyanines with thiophene ring in the chromene part of molecules were also synthesized.

EXPERIMENT

^{1}H NMR spectra were recorded on Bruker WM-250 and Bruker AM-300 instruments. Mass spectra were obtained on a Kratos spectrometer (70 eV) with direct sample injection into the ion source. Melting points were measured on a Boetius hot stage and were not corrected. Electronic absorption spectra were recorded on a Varian Cary-100 spectrophotometer. The irradiation of solutions was carried out with the light of a high-pressure mercury lamp DRSh-250 equipped with a set of interference filters. Commercially available (Aldrich) anhydrous methanol (99.9%) and ethanol (99.99%) were used for synthesis, and the highest grade solvents (Fluka) were used for spectroscopic measurements.

General Procedure for the Spiro Compounds Synthesis

To a stirred solution of the Fischer's salt (2.5 mmol) and salicylic aldehyde or its analog (2.5 mmol) in methanol (3 ml) triethylamine (2.5 mmol) was added. After refluxing for 20 min (TLC control) the solvent was removed under reduced pressure. The residue was purified by chromatography.

Crystallographic Studies

The crystallographic data were measured on a Bruker diffractometer SMART 1000 CCD using Mo K_α ($\lambda = 0.71073$ Å) radiation. Direct methods. Full-matrix least squares refinement with all anisotropic non-hydrogen atoms and hydrogen atoms in calculated positions. Programs SMART, SAINTPlus, SHELXTL [7] were used. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center. **11**: $C_{22}H_{22}N_2OS$, M = 362.48, monoclinic, space group $P2_1/c$, $a = 6.557(2)$ Å, $b = 24.603(7)$ Å, $c = 11.590(3)$ Å, $\beta = 90.688(6)^\circ$, $V = 1869.7$ Å^3, $Z = 4$, $D_{calcd} = 1.288\,g\,cm^{-3}$, $T_{mel} = 92-93^\circ C$, 4080 unique reflections ($1.94 \leq \theta \leq 26.99^\circ$), R ($R_w$) = 0.074 (0.177). **13**: $C_{24}H_{20}N_2OS$, M = 384.48, monoclinic, space group Cc, $a = 12.083(4)$ Å, $b = 16.809(5)$ Å, $c = 10.651(3)$ Å, $\beta = 121.838(5)^\circ$, $V = 1837.8$ Å^3, $Z = 4$, $D_{calcd} = 1.390\,g\,cm^{-3}$, $T_{mel} = 225^\circ C$, 4548 unique reflections ($2.40 \leq \theta \leq 23.67^\circ$), R ($R_w$) = 0.143 (0.088).

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