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Isomerization of 3*H*- to 2*H*-[1]Benzothieno[3,2-*b*]pyrroles and Synthesis of the First Merocyanine Dyes Based on Them

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New 2*H*-[1]benzothieno[3,2-*b*]pyrroles were synthesized by a [1,5]-sigmatropic shift of 3*H*-benzothienopyrroles. The dependence of the rearrangement on solvent and temperature was studied. The first merocyanine dyes based on both 3*H*- and 2*H*-benzothienopyrroles were synthesized and characterized by NMR- and UV/Vis spectroscopy, mass spectrometry, and X-ray crystallography.

Introduction

Merocyanine dyes have attracted much attention as nonlinear optical chromophores for photorefractive (PR) materials.[1] The potential applications of PR materials include optical filters, holographic data storage, image processing, and phase conjugation. Recently, we developed a convenient method for the synthesis of 3*H*-thieno[3,2-*b*]pyrrole and 3*H*-[1]benzothieno[3,2-*b*]pyrrole derivatives under Fisher reaction conditions and prepared the first spiropyrans and spirooxazines based on them.[2] As a continuation of our studies, we were interested in the preparation of novel merocyanine dyes of the 1-benzothieno[3,2-*b*]pyrrole series that could be considered as open forms of the spiropyrans.

Results and Discussion

It was expected that the reaction of the pyrrolenine **1a**[2a] with methyl triflate followed by condensation with aldehyde **4** would lead to merocyanine dye **5** as a single product (Scheme 1). However, along with compound **5** we have isolated its structural isomer **6**. It might be supposed that salt **2**, which results from the alkylation of pyrrolenine, rearranges to compound **3** by a [1,5]-sigmatropic shift of a methyl group. In a manner similar to **2**, salt **3** condenses with aldehyde **4** to give the isomeric merocyanine dye **6**. While the merocyanine **5** is red, its isomer **6** is blue (in ethanol solution, the absorption maxima are 553 and 677 nm, respectively). The 124-nm red shift is explained by an extra double bond between the nitrogen atom and the carbonyl group in merocyanine **6**.

The structure of the blue isomer **6** was proved by X-ray crystallography (Figure 1). The merocyanine molecule has a planar structure with *Z*,*Z* configuration of the double bonds. The C3–C12 (1.392 Å), C12–C13 (1.394 Å), and C13–C2′ (1.409 Å) bond lengths are almost equal, which means that molecule **6** has a high degree of double-bond conjugation.

The structure of compound **5** was proved by ^{1}H-, ^{13}C-, NOE-, COSY-, and HMBC NMR spectroscopy and mass spectrometry, and it was confirmed by elemental analysis. Cross peaks of a methine proton at δ = 8.50 ppm with C-3′ (δ = 167.54 ppm) and C-2 (δ = 178.78 ppm), and cross peaks of another methine proton at δ = 6.44 ppm with C-2′ (δ = 117.18 ppm) and C-3 (δ = 51.35 ppm) were observed in the 2D HMBC spectrum (Figure 2). Thus the lower-field signal (δ = 8.50 ppm) was assigned to 13-H, whilst the higher-field signal at δ = 6.44 ppm was assigned to 12-H. This conclusion corresponds perfectly with literature data,[3] where the structure of the merocyanine form of spirobenzothiopyran was independently proved by using deuterium labeling. In the NOE spectrum, cross peaks of 13-H with CMe_2 and 12-H with NMe are observed (Figure 3). This allows one to conclude that the double bond of the pyrrole moiety possesses an *E* configuration.

Using HMBC and COSY spectra, we determined the positions of all the aromatic protons for merocyanines **5** and **6**. There are two ABCD proton systems in 1-benzothieno[3,2-*b*]pyrrole and 1-benzothiophen-3-one with equal

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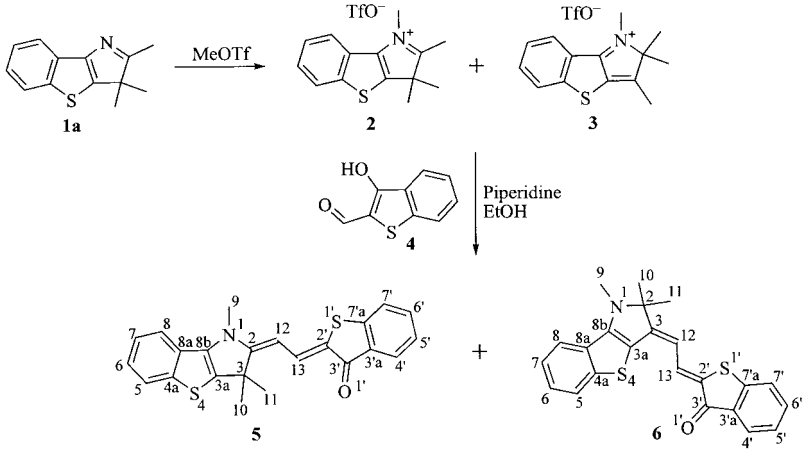


Scheme 1.

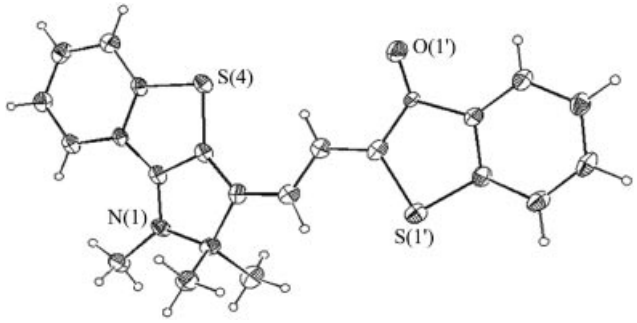


Figure 1. Molecular structure of the cyanine dye **6**. Ellipsoids are drawn at the 20% probability level.

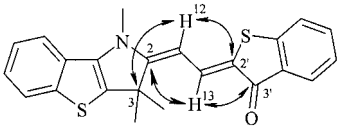


Figure 2. HMBC interactions in cyanine **5**.

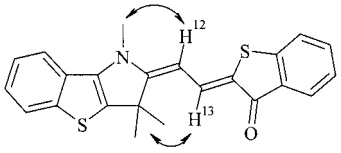


Figure 3. NOESY interactions in cyanine **5**.

coupling constants J_{AB} = 7.9, J_{BC} = 7.3, J_{CD} = 7.9 Hz.[4] The extensive NMR studies enabled us to prove the configuration of the double bond near the pyrrole cycle and thus to decrease the possible number of isomers of **5** to two (*E*,*Z* and *E*,*E*, Figure 4).

MNDO calculations that were carried out for the four possible isomers of **5** showed that the *E*,*Z* form is the most stable, while the second possible isomer (*E*,*E*) has the second highest enthalpy (Table 1). The calculated results correspond to the gas phase, but because of the high dipole moment (6.20 D) of the *E*,*Z* isomer, it might be expected that this isomer would be more stable in polar solvents as well. The stability of the *E*,*Z* form of the merocyanine **5** agrees with literature data from the calculation for the merocyanine form of spiropyrans,[5] though the existence of both *E*,*Z* and *E*,*E* isomers was proved experimentally.[6] In spite of the lack of direct proof it could be asserted that the double bonds of the cyanine **5** have *E*,*Z* configuration.

Table 1. MNDO quantum calculations for cyanine **5**.

	E,*Z*	*E*,*E*	*Z*,*Z*	*Z*,*E*
$\Delta H_f°$ [kJ/mol]	300.91	313.80	305.59	315.77
μ, [D]	6.20	2.17	2.24	5.55

This conclusion corresponds to the comparison of the structure of dye **5** with that of its indoline analog **8** prepared

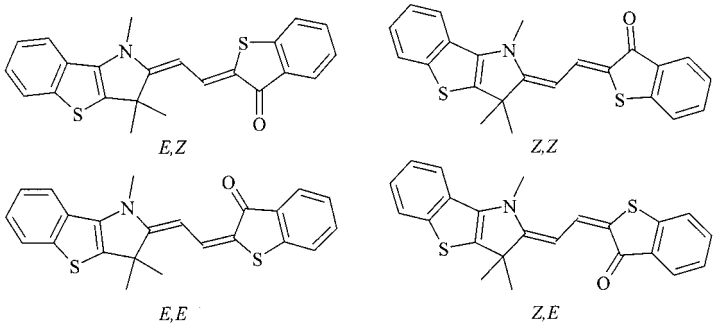
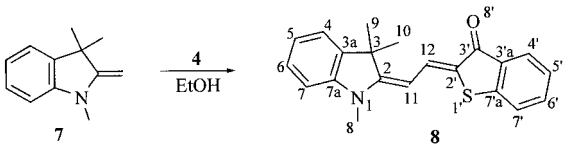


Figure 4. Possible isomers of cyanine **5**.

by a similar method from 1,3,3-trimethyl-2-methyleneindoline (**7**) and aldehyde **4** (Scheme 2).



Scheme 2.

X-ray analysis of the red-colored dye **8** shows that the molecule has an almost planar structure (the dihedral angle between the indole and the benzothiophenone fragments is 8.73°) and that the double bonds have *E*,*Z* geometry (Figure 5). The distribution of the double bonds is close to quinoidal.

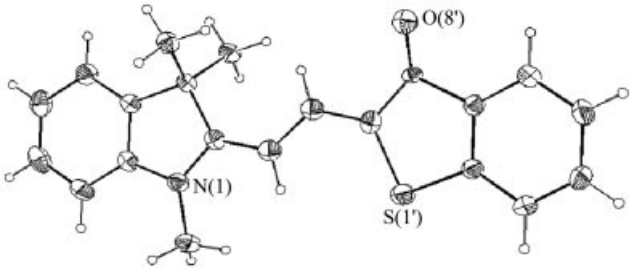
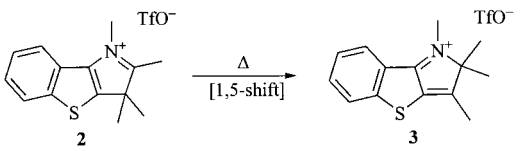


Figure 5. Molecular structure of the cyanine dye **8**. Ellipsoids are drawn at the 20% probability level.

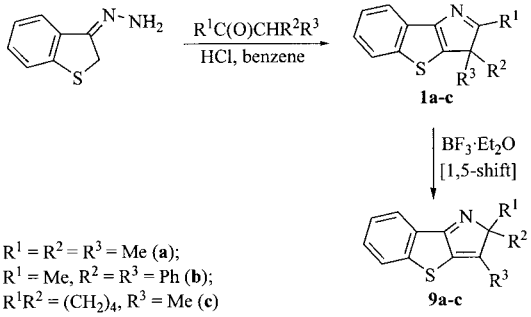
Our further investigations were connected with the study of the rearrangement reaction. We have found that the yields of the merocyanine dyes **5** and **6** are critically dependent on the alkylation reaction time. Heating of the pyrrolenine **1a** with methyl triflate in acetonitrile for 2–3 h led substantially to the formation of the red dye **5** (53%), whereas the yield of the blue isomer **6** was only 2–3%. When the reaction time was increased to 23 h, the yields of the dyes **5** and **6** were 18% and 29%, respectively. Finally, when the reaction mixture was refluxed for 32 h, the yield of the blue-colored cyanine **6** reached 50%, with only a trace of dye **5**. Thus both red and blue merocyanines could be obtained by varying the reaction time.

Then, we have studied the rearrangement of salt **2** (Scheme 3). The heating of the latter in benzene for 30–35 h led to the isomeric compound **3**, which was characterized by ^{1}H NMR spectroscopy and elemental analysis. We have found that the increase in temperature reduces the reaction time, and the transformation of salt **2** into compound **3** is complete within 2.5 h when the reactant is refluxed in *p*-xylene (138–140 °C).



Scheme 3.

We supposed that, not only the quaternary salt **2**, but also 3*H*-thienopyrroles could undergo rearrangement in the presence of Lewis acids. In fact, the use of boron trifluoride–diethyl ether as catalyst allowed us to obtain the isomeric 2*H*-thienopyrroles **9a**–**c** as free bases (Scheme 4). The starting 3*H*-pyrroles **1a**–**c** were synthesized from 1-benzothiophen-3-one hydrazone by a method developed earlier in our group.[2a]



Scheme 4.

It was found that, of all the 3*H*-benzothienopyrroles synthesized, the diphenyl derivative **1b** was the most reactive because of both electronic and steric effects. The rearrangement occurs in benzene or THF in the presence of $BF_3{\cdot}OEt_2$ at 25 °C, leading to **9b** in high yield. The reaction time is significantly shorter in THF than in benzene. To eliminate possible ionic pathways for the rearrangement, we heated 2-methyl-3,3-diphenyl-3*H*-pyrrole **1b** in *p*-xylene (138–140 °C) without catalyst. The reaction progressed indeed, but took more time to complete than in the presence of catalyst and was accompanied by significant resinification.

The structure of the rearranged product **9b** was proved by X-ray crystallography (Figure 6). The phenyl ring in position 3 is rotated by 12.63° relative to the benzothienopyrrole plane. The N1–C8b (1.288 Å) and C3–C3a (1.351 Å)

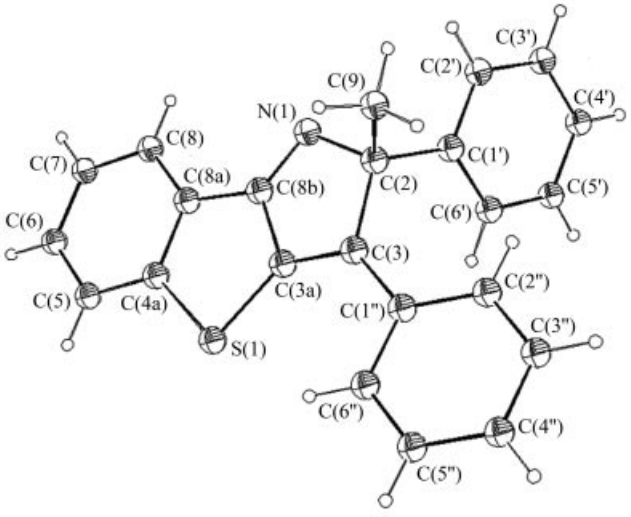
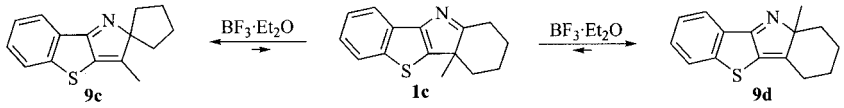


Figure 6. Molecular structure and atom labeling of the 2*H*-benzothienopyrrole **9b**. Ellipsoids are drawn at the 20% probability level.



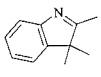
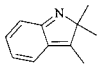
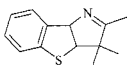
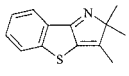
Scheme 5.

bond lengths in the pyrrole ring are close to the length of a classical double bond, and the C3a–C8b (1.460 Å) bond length corresponds to that of an ordinary single bond. This implies that the thiophene ring is not aromatic.

Trimethylthienopyrrole **1a** does not undergo the rearrangement at ambient temperature. However, the reaction proceeds when refluxed in benzene for 28–30 h, and the reaction time is reduced to 1 h in *p*-xylene at 138–140 °C. An interesting result was observed for tetrahydroindole **1c** under similar conditions. It was found that **1c** rearranges to give the spiro product **9c** in 1 h at 80 °C. Increasing the reaction time or raising the temperature up to 138–140 °C leads to 1-benzothieno[3,2-*b*]indole **9d** through the migration of a methyl group (Scheme 5). Apparently, spiro compound **9c** is a kinetic, and tetrahydroindole **9d** is a thermodynamic product. The structures of the compounds **9c** and **9d** were proved by ^{1}H- and ^{13}C NMR spectroscopy and mass spectrometry, and they were confirmed by elemental analysis of their picrate salts.

This reaction belongs to the Wagner–Meerwein type rearrangement and proceeds through a [1,5]-sigmatropic shift to the 3*H*-[1]benzothieno[3,2-*b*]pyrrole system. In the literature, there are several examples of such rearrangements of 3*H*-pyrroles having alkyl, aryl, and carboxylic ester groups at C-3;[7] however, there is no information on the rearrangement of 3*H*-indole derivatives. Our attempts to carry out the rearrangement of 2,3,3-trimethyl-3*H*-indole under similar conditions failed, and prolonged refluxing in *p*-xylene in the presence of boron trifluoride–diethyl ether led to the starting compound only. In order to clarify this observation, we performed the DFT quantum calculations of the standard enthalpy of formation of different condensed and uncondensed 2*H*- and 3*H*-pyrrole systems (Table 2). The calculated results show that this rearrangement should be possible in the case of pyrrole (ΔH_{3H-2H} = +15.62 kJ/mol) but not indole derivatives (ΔH_{3H-2H} = –80.21 kJ/mol). This is also confirmed by literature data: the reaction of trialkoxy-3*H*-indole with methyllithium leads to 2,2-dimethyl-3-methyleneindoline instead of 2,2,3-trimethyl-2*H*-indole, which shows the instability of the quinoidal 2*H*-indole form.[8] The calculated energy differences between 3*H*- and 2*H*-(benzo)thienopyrroles are negative but relatively small; therefore, the 3*H*-isomers should be more stable, but the rearrangement is possible.

Table 2. Quantum calculations for 3*H*- and 2*H*- pyrrole derivatives (DFT B3LYP/6-31G**).

3*H*	E_{3H}–E_{2H} [kJ/mol]	2*H*
	–80.21	
	–14.75	
	–0.69	
	+15.62	

Both 2*H*- and 3*H*-thienopyrrole derivatives should be stored at low temperature (–5 to –10 °C), except diphenyl-substituted **1b** and **9b** that are quite stable at normal conditions. For all the rearranged products **9a**–**c** the signals of the alkyl protons in the ^{1}H NMR spectra are shifted upfield relative to those of the starting 3*H*-pyrrole derivatives. The main difference in the ^{13}C NMR spectra of 3*H*- and 2*H*-pyrroles is an expected large downfield shift of the quaternary carbon atom signal due to bonding with the nitrogen atom. For instance, the rearrangement of pyrrolenine **1a** to **9a** leads to a shift of the signal of the *C*Me$_2$ carbon atom from 49.60 to 87.29 ppm. The same is true for merocyanines **5** and **6** (the *C*Me$_2$ signal is shifted from 51.35 to 84.68 ppm).

Conclusion

In conclusion, we have observed the Wagner–Meerwein type rearrangement in benzothienopyrrole derivatives and shown that this reaction depends on both solvent and temperature. Novel 2*H*-[1]benzothieno[3,2-*b*]pyrrole derivatives and the first merocyanine dyes of the 2*H*- and 3*H*-benzothienopyrrole series have been synthesized.

Experimental Section

NMR spectra (^{1}H-, ^{13}C-, and 2D experiments) were recorded with Bruker DRX-500, AM-300, WM-250, or AC-200 spectrometers. Mass spectra were obtained with 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. Electronic absorption spectra were recorded on a LOMO SF-256UVI spectrophotometer. Column chromatography was performed by 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. 3-Hydroxy-1-benzothiophene-2-carbaldehyde (**4**) was prepared by a known procedure.[9]

3*H*-[1]Benzothieno[3,2-*b*]pyrroles were synthesized by a method developed earlier[2a] from 1-benzothiophen-3-one hydrazone (1 g, 6.1 mmol) and a suitable ketone (6.1 mmol) in anhydrous benzene (30 mL). The products were purified by column chromatography ($CHCl_3$/ethyl acetate, 3:1) or by recrystallization from ethanol.

2-Methyl-3,3-diphenyl-3*H*-[1]benzothieno[3,2-*b*]pyrrole (1b): Yield 0.56 g (27%). M.p. 181–183 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C): δ = 2.41 (s, 3 H, Me), 7.18–7.25 (m, 4 H, Ph), 7.29–7.37 (m, 7 H, Ph + H-arom.), 7.47 (t, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 8.1 Hz, 1 H, H-arom.), 7.79 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, H-arom.), 8.14 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, H-arom.) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 24 °C): δ = 18.51 (Me), 72.99 (C-3), 121.59, 123.91, 124.30, 125.01, 127.79, 127.99, 129.02, 130.30, 140.15, 144.08, 144.60, 151.87, 187.81 (C-2) ppm. MS: *m*/*z* = 339 [M$^+$]. $C_{23}H_{17}NS$ (339.45): calcd. C 81.38, H 5.05, N 4.13; found C 80.76, H 5.04, N 4.16.

4a-Methyl-2,3,4,4a-tetrahydro-1*H*-[1]benzothieno[3,2-*b*]indole (1c): Yield 0.59 g (40%). M.p. 103–104 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 24 °C): δ = 1.15–1.28 (m, 1 H, CH), 1.30 (s, 3 H, Me), 1.32–1.49 (m, 1 H, CH), 1.52–1.71 (m, 2 H, CH_2), 2.02–2.16 (m, 1 H, CH), 2.16–2.28 (m, 1 H, CH), 2.51 (td, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 5.9 Hz, 1 H, CH), 2.81–2.93 (m, 1 H, CH), 7.24 (t, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.), 7.38 (t, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.), 7.76 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.), 8.08 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 24 °C): δ = 20.23, 21.36, 29.70, 30.41, 39.66, 55.21 (C-3), 121.14, 123.85, 123.90, 124.79, 130.50, 143.51, 144.51, 151.42, 192.32 (C-2) ppm. MS: *m*/*z* = 241 [M$^+$]. $C_{15}H_{15}NS$ (241.35): calcd. C 74.65, H 6.26, N 5.80; found C 74.29, H 6.59, N 5.88.

1,2,3,3-Tetramethyl-3*H*-[1]benzothieno[3,2-*b*]pyrrol-1-ium Trifluoromethanesulfonate (2): A solution of 3*H*-pyrrole **1a** (0.3 g, 1.4 mmol) and methyl trifluoromethanesulfonate (0.16 mL, 1.4 mmol) in acetonitrile (3 mL) was refluxed for 20 min, then cooled, and the solvent was evaporated. The crude solid was washed with THF and dried. Yield 0.4 g (75%). ^{1}H NMR (250 MHz, [D$_6$]DMSO, 24 °C): δ = 1.64 (s, 6 H, CMe_2), 2.78 (s, 3 H, Me), 4.27 (s, 3 H, NMe), 7.55 (t, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1 H, H-arom.), 7.63 (t, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1 H, H-arom.), 8.21 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.), 8.27 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.) ppm. $C_{15}H_{16}F_3NO_3S_2$ (379.42): calcd. C 47.48, H 4.25, N 3.69; found C 47.25, H 4.39, N 3.47.

1,2,2,3-Tetramethyl-2*H*-[1]benzothieno[3,2-*b*]pyrrol-1-ium Trifluoromethanesulfonate (3): A suspension of salt **2** (0.2 g, 0.53 mmol) in *p*-xylene (2 mL) was refluxed for 2.5 h. After cooling, the solid was filtered off, washed with benzene, and dried in vacuo. Yield 0.12 g (60%). ^{1}H NMR (250 MHz, [D$_6$]DMSO, 24 °C): δ = 1.56 (s, 6 H, CMe_2), 2.38 (s, 3 H, Me), 3.90 (s, 3 H, NMe), 7.64 (t, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1 H, H-arom.), 7.92 (t, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1 H, H-arom.), 8.09 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.), 8.49 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.) ppm. $C_{15}H_{16}F_3NO_3S_2$ (379.42): calcd. C 47.48, H 4.25, N 3.69; found C 47.23, H 4.41, N 3.44.

2-[2-(1,3,3-Trimethyl-1,3-dihydro-2*H*-[1]benzothieno[3,2-*b*]pyrrol-2-yliden)ethylidene]-1-benzothiophen-3-one (5): Methyl trifluoromethanesulfonate (0.26 mL, 2.3 mmol) was added to a stirred solution of pyrrolenine **1a** (0.5 g, 2.3 mmol) in MeCN (5 mL). The reaction mixture was refluxed for 3 h, then cooled, and the solvent was removed under vacuum. The brownish solid was dissolved without purification in EtOH (5 mL), and after aldehyde **4** (0.41 g, 2.3 mmol) and piperidine (0.23 mL, 2.3 mmol) were added, the solution was refluxed for 1 h. The reaction mixture was cooled, and the solid precipitated was filtered off, washed with EtOH and dried. The filtrate was evaporated, and the crude product was purified by column chromatography, by being eluted with $CHCl_3$/ethyl acetate, 3:1. Total yield 0.48 g (53%). M.p. 239–241 °C (ethanol). UV/Vis: λ_{max}, nm (log ε) = 553 (4.74) in ethanol, 540 (4.67) in acetonitrile. ^{1}H NMR (250 MHz, [D$_6$]DMSO + CF_3COOH, 24 °C): δ = 1.84 (s, 6 H, CMe_2), 4.14 (s, 3 H, NMe), 6.44 (d, $^3J_{HH}$ = 15.3 Hz, 1 H, 12-H), 7.42 (t, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.9 Hz, 1 H, 6′-H), 7.49 (t, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.9 Hz, 1 H, 6-H), 7.57 (t, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1 H, 7-H), 7.60 (t, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.9 Hz, 1 H, 5′-H), 7.86 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 4′-H), 7.92 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 7′-H), 8.14 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 5-H), 8.26 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 8-H), 8.50 (d, $^3J_{HH}$ = 15.3 Hz, 1 H, 13-H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO + CF_3COOH, 24 °C): δ = 27.34 (C-10, C-11), 35.19 (C-9), 51.35 (C-3), 103.41 (C-12), 117.18 (C-2′), 120.91, 123.74, 124.16, 125.05, 125.10, 125.31, 125.58, 125.73, 128.21, 131.32, 132.44, 137.41 (C-13), 138.10, 140.46, 142.67, 167.54 (C-3′), 178.78 (C-2) ppm. MS: *m*/*z* = 389 [M$^+$]. $C_{23}H_{19}NOS_2$ (389.54): calcd. C 70.92, H 4.92, N 3.60; found C 70.51, H 5.17, N 3.87.

2-[2-(1,2,2-Trimethyl-1,2-dihydro-3*H*-[1]benzothieno[3,2-*b*]pyrrol-3-yliden)ethylidene]-1-benzothiophen-3-one (6): A solution of 3*H*-pyrrole **1a** (0.5 g, 2.3 mmol) and methyl trifluoromethanesulfonate (0.26 mL, 2.3 mmol) in acetonitrile (5 mL) was refluxed for 32 h. The solvent was evaporated, and to the brownish solid were added ethanol (5 mL), aldehyde **4** (0.41 g, 2.3 mmol) and piperidine (0.23 mL, 2.3 mmol). The reaction mixture was heated to reflux for 1 h, cooled and filtered to give the blue solid **6** (0.16 g, 18%). Ethanol was evaporated from the solution, and the crude product was purified by column chromatography (eluent $CHCl_3$/ethyl acetate, 3:1). Total yield 0.45 g (50%). M.p. 233–235 °C (ethanol). UV/Vis: λ_{max}, nm (log ε) = 640 (4.56), 677 (4.62) in ethanol, 621 (4.44), 656 (4.43) in acetonitrile. ^{1}H NMR (250 MHz, [D$_6$]DMSO + CF_3COOH, 24 °C): δ = 1.70 (s, 6 H, CMe_2), 3.90 (s, 3 H, NMe), 6.75 (d, $^3J_{HH}$ = 15.3 Hz, 1 H, 12-H), 7.42 (t, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.9 Hz, 1 H, 5′-H), 7.50 (t, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.9 Hz, 1 H, 6′-H), 7.64 (t, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1 H, 7-H), 7.84 (d, $^3J_{HH}$ = 15.3 Hz, 1 H, 13-H), 7.84–7.94 (m, 2 H, 6-H and 7′-H), 7.99 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 4′-H), 8.16 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 5-H), 8.49 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO + CF_3COOH, 24 °C): δ = 21.34 (C-10, C-11), 31.93 (C-9), 84.68 (C-2), 113.44 (C-12), 116.22 (C-2′), 122.39, 122.86, 123.38, 124.88, 125.73, 126.08, 126.97, 128.63, 129.17, 132.24, 134.00 (C-13), 135.74, 137.90, 152.71, 155.06 (C-3′), 161.28 (C-3), 169.27 ppm. MS: *m*/*z* = 389 [M$^+$]. $C_{23}H_{19}NOS_2$ (389.54): calcd. C 70.92, H 4.92, N 3.60; found C 70.53, H 5.23, N 3.56.

2-[2-(1,3,3-Trimethyl-1,3-dihydro-2*H*-indol-2-yliden)ethylidene]-1-benzothiophen-3-one (8): A solution of 1,3,3-trimethyl-2-methyleneindoline (1 mL, 5.5 mmol) and aldehyde **4** (1 g, 5.6 mmol) in ethanol (10 mL) was refluxed for 1.5 h. After cooling, the greenish yellow crystals were filtered off, washed with ethanol and dried. Yield 1.37 g (73%). M.p. 203–205 °C (ref.[10] 201 °C). UV/Vis: λ_{max}, nm (log ε) = 520 (4.76) in acetonitrile. ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C): δ = 1.70 (s, 6 H, CMe_2), 3.33 (s, 3 H, NMe), 5.48 (d, $^3J_{HH}$ = 13.2 Hz, 1 H, 11-H), 6.82 (d, $^3J_{HH}$ = 7.4 Hz, 1 H, H-arom.), 7.03 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, H-arom.), 7.20–7.30 (m, 3 H, H-arom.), 7.46–7.54 (m, 2 H, H-arom.), 7.93 (d, $^3J_{HH}$ = 7.4 Hz, 1 H, H-arom.), 8.25 (d, $^3J_{HH}$ = 13.2 Hz, 1 H, 12-H) ppm.

2*H*-[1]Benzothieno[3,2-*b*]pyrroles (General Procedure): Boron trifluoride–diethyl ether (0.39 mmol) was added to a stirred solution of 3*H*-pyrrole **1** (0.3 mmol) in benzene or xylene (3 mL). The reaction mixture was refluxed until the starting material disappeared. The solution was poured into water (30 mL), and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). After evaporation of the solvent in vacuo, the crude product was purified by column chromatography ($CHCl_3$/ethyl acetate, 3:1). For analytical purposes picrate salts were prepared by the reactions of 2*H*-pyrroles **9** with 2,4,6-trinitrophenol in ethanol.

2,2,3-Trimethyl-2*H*-[1]benzothieno[3,2-*b*]pyrrole (9a): Yield 26 mg (40%). Brownish oil. ^{1}H NMR (250 MHz, $CDCl_3$, 24 °C): δ = 1.38

(s, 6 H, CMe_2), 2.08 (s, 3 H, Me), 7.28 (t, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1 H, H-arom.), 7.42 (t, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1 H, H-arom.), 7.48 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.), 8.04 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 24 °C): δ = 12.13 (Me), 22.77 (CMe_2), 87.19 (C-2), 124.41, 124.61, 125.00, 125.32, 126.58, 131.60, 150.32, 157.74, 174.15 ppm. MS: *m*/*z* = 215 [M$^+$]. Picrate: m.p. 227–229 °C (ethanol). $C_{19}H_{16}N_4O_7S$ (444.42): calcd. C 51.35, H 3.63, N 12.61; found C 50.93, H 3.84, N 12.40.

3-Methyl-2,3-diphenyl-2*H*-[1]benzothieno[3,2-*b*]pyrrole (9b): Yield 92 mg (90%). M.p. 135–137 °C (ethanol). ^{1}H NMR (250 MHz, $CDCl_3$, 24 °C): δ = 2.03 (s, 3 H, Me), 7.20–7.40 (m, 11 H, 2Ph + H-arom.), 7.50 (t, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1 H, H-arom.), 7.58 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.), 8.14 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 24 °C): δ = 21.89 (Me), 90.98 (C-2), 121.41, 124.18, 125.12, 125.75, 125.94, 127.64, 127.80, 127.92, 128.01, 128.60, 128.80, 128.86, 131.68, 131.90, 138.70, 156.28, 174.35 ppm. MS: *m*/*z* = 339 [M$^+$]. $C_{23}H_{17}NS$ (339.45): calcd. C 81.38, H 5.05, N 4.13; found C 81.15, H 5.40, N 4.04.

3-Methylspiro[2*H*-[1]benzothieno[3,2-*b*]pyrrole-2,1′-cyclopentane] (9c): Yield 21 mg (29%). M.p. 113–115 °C (ethanol). ^{1}H NMR (250 MHz, $CDCl_3$, 24 °C): δ = 1.67–1.84 (m, 2 H, CH_2), 1.85–2.02 (m, 4 H, CH_2), 2.07 (s, 3 H, Me), 2.13–2.34 (m, 2 H, CH_2), 7.26 (t, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1 H, H-arom.), 7.40 (t, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.3 Hz, 1 H, H-arom.), 7.46 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.), 8.11 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 24 °C): δ = 12.17, 26.38, 34.09, 97.93 (C-2), 124.42, 125.16, 125.30, 127.99, 129.50, 131.50, 150.25, 154.44, 174.05 ppm. MS: *m*/*z* = 241 [M$^+$]. Picrate: m.p. 183–185 °C (ethanol). $C_{21}H_{18}N_4O_7S$ (470.46): calcd. C 53.61, H 3.86, N 11.91; found C 53.55, H 4.05, N 11.99.

10a-Methyl-2,3,4,10a-tetrahydro-1*H*-[1]benzothieno[3,2-*b*]indole (9d): Yield 49 mg (67%). M.p. 121–123 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C): δ = 1.01 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 4.4 Hz, 1 H, CH), 1.14 (qt, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 4.4 Hz, 1 H, CH), 1.34 (s, 3 H, Me), 1.62 (qt, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.7 Hz, 1 H, CH), 1.72–1.82 (m, 1 H, CH), 1.99–2.10 (m, 1 H, CH), 2.32 (td, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 5.5 Hz, 1 H, CH), 2.46–2.56 (m, 1 H, CH), 2.83–2.92 (m, 1 H, CH), 7.29 (t, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.8 Hz, 1 H, H-arom.), 7.43 (t, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.8 Hz, 1 H, H-arom.), 7.49 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.), 8.07 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-arom.) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 24 °C): δ = 19.93, 22.24, 26.77, 27.89, 39.22, 86.60 (C-2), 124.48, 124.96, 125.31, 125.73, 127.90, 131.52, 150.44, 160.73, 174.66 ppm. MS: *m*/*z* = 241 [M$^+$]. Picrate: m.p. 213–214 °C (ethanol). $C_{21}H_{18}N_4O_7S$ (470.46): calcd. C 53.61, H 3.86, N 11.91; found C 53.10, H 4.04, N 11.83.

X-ray Crystallography: X-ray diffraction data were collected with a Syntex $P2_1$ diffractometer with graphite-monochromated Mo-K_α radiation in the $\theta/2\theta$ scan mode. The structures were solved by direct methods and refined by full-matrix least-squares in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were located by difference synthesis and refined isotropically by least-square methods.

Siemens P3/PC[11] and SHELXTL PLUS 5[12] programs were used. CCDC-290196 (for **6**), -290288 (for **8**) and -290289 (for **9b**) 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.

Crystal Data for 6: $C_{23}H_{19}NOS_2$, M_r = 389.51, rhombic, space group *Pbca*, *a* = 11.866(6), *b* = 16.114(6), *c* = 20.058(7) Å, *V* = 3835(3) Å^3, *T* = 100(2) K, *Z* = 8, $D_{calcd.}$ = 1.349 g/cm^3, 2950 unique reflections in the $2.36 \leq \theta \leq 24.00°$ range. The final *R* factors: R_1 = 0.074, wR_2 = 0.115 (all data).

Crystal Data for 8: $C_{21}H_{19}NOS$, M_r = 333.43, monoclinic, space group $P2_1/c$, *a* = 8.286(3), *b* = 12.582(4), *c* = 16.963(6) Å, β = 102.22(3)°, *V* = 1728.5 Å^3, *T* = 100(2) K, *Z* = 4, $D_{calcd.}$ = 1.281 g/cm^3, 3051 unique reflections in the $2.94 \leq \theta \leq 25.04°$ range. The final *R* factors: R_1 = 0.067, wR_2 = 0.170 (all data).

Crystal Data for 9b: $C_{23}H_{17}NS$, M_r = 339.45, rhombic, space group *Pbca*, *a* = 15.241(4), *b* = 7.996(2), *c* = 28.454(7) Å, *V* = 3467.56 Å^3, *T* = 193(2) K, *Z* = 8, $D_{calcd.}$ = 1.300 g/cm^3, 3960 unique reflections in the $2.94 \leq \theta \leq 25.04°$ range. The final *R* factors: R_1 = 0.076, wR_2 = 0.113 (all data).

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