REARRANGEMENT OF SUBSTITUTED 2,4,4,6-TETRAARYL-4*H*-THIOPYRANS TO TRIARYL-3a*H*-BENZO[3,4]CYCLOPENTA[1,2-*b*]THIOPHENE

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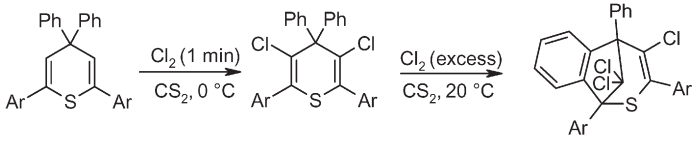
An intensive bromination of 2,6-diaryl-4,4-diphenyl-4*H*-thiopyrans can lead through 3,5-dibromo derivatives to unexpected 2,8-diaryl-3-bromo- and 2,8-diaryl-3,5-dibromo-3a-phenyl-3a*H*-benzo[3,4]cyclopenta[1,2-*b*]thiophene as demonstrated on examples where the respective aryl groups are phenyl or 4-fluorophenyl. On the other hand, analogous spiro-[fluorene-9,4′-thiopyran]s do not exhibit the rearrangement evidently due to a rigid conformation of the fluorene moiety. The reaction mechanism for the rearrangement is proposed.
Keywords: Thiopyrans; Bromination; Benzo[3,4]cyclopenta[1,2-*b*]thiophene; Thiapentalene; Rearrangements; Sulfur heterocycles.

The 2,4,4,6-tetraaryl-4*H*-thiopyrans are interesting substances capable to undergo color changes caused by illumination in the solid state[1]. An alternative way how to modify the parent 2,4,4,6-tetraphenyl-4*H*-thiopyran skeleton is introduction of substituents to positions 3 and 5. A high reactivity of the heterocycle towards electrophilic agents[2,3] may result in unusual ring transformations affording products of unexpected structures. Thus, a rearrangement of 2,4,4,6-tetraaryl-4*H*-thiopyrans through a 3,5-dichloro derivative intermediate to trichloro bicycles has been observed[4] after prolonged chlorination at room temperature (Scheme 1). Although a similar 3,5-bromination has also been reported[3], no analogous tandem rearrangement has yet been investigated. In this paper we present new results showing that a prolonged intensive bromination of 2,6-diaryl-4,4-diphenyl-

4*H*-thiopyrans **1** and **2** leads to rearranged products the structures of which significantly differ from those of the aforementioned chlorination[4] sequence. In addition, it is also demonstrated that spirocyclic 4*H*-thiopyran **3** behaves differently affording no rearranged products during bromination.



SCHEME 1
Chlorine-induced isomerization of 2,4,4,6-tetraaryl-4*H*-thiopyrans[4]

RESULTS AND DISCUSSION

Preparation of compounds[1c] **1**–**3** as well as bromination[3] of **1** giving **4** have been described previously. It has been established that fluoro derivative **2** and the spiro-4*H*-thiopyran **3** can be converted to the corresponding 3,5-dibromo derivatives **5** and **6** under similar conditions (3 equivalents of Br_2, starting at 0 °C). However, if the brominations were carried out with a large excess of bromine (8 equivalents of Br_2) in substantially smaller amounts of carbon disulfide at 20 °C, 4*H*-thiopyran **1** gave a mixture containing two substances in addition to minor amounts of 3,5-dibromo derivative **4**. Analogous bromination of 4*H*-thiopyran **2** led to a mixture composed of two products (1:1, HPLC) and a minor amount of 3,5-dibromo derivative **5**. Finally, by more intensive bromination (10 equivalents of Br_2), 4*H*-thiopyran **2** gave a high yield of single compound (67% yield, after separation), which was entirely different from 3,5-dibromo derivative **5**. Furthermore, comparative bromination experiments on analytical scale (HPLC) with dibromo derivative **4** showed that the same substances were formed. NMR investigations indicated that new compounds obtained by intensive bromination exhibit the same skeleton of a lower molecular symmetry in comparison with 3,5-dibromo derivatives **4** and **5**.

The X-ray structure of unexpected product given in Fig. 1 revealed that the investigated crystalline substance was in fact 3,5-dibromo-2,3a,8-triphenyl-3a*H*-benzo[3,4]cyclopenta[1,2-*b*]thiophene (**7**) (Scheme 2). Hence, it could be concluded that the second compound present in the reaction mixture which was isolated by preparative TLC from mother liquors (see Experimental) possesses the formula **8**. Analogously, formula **9** can be assigned to rearranged product from 4*H*-thiopyran **2**. Consequently, it was obvious that the first bromination of fluoro derivative **2** (8 equivalents of Br_2) afforded

mixture of **9** and plausible intermediate **10** (vide supra), but the compound **10** was not isolated. NMR data of compounds **7**–**9** agree with these structures. Detailed analysis of **9** in which phenyls attached to C-2 and C-6 were labeled by fluorine clearly revealed the fate of all phenyl groups. This conclusion was further supported by partial catalytic hydrogenation of 3,5-dibromo derivative **7** on a Pd catalyst affording 3-bromo derivative **8** under hydrogenolysis of the less sterically hindered bromine in position 5 (Scheme 2).

It is easily recognizable that hydrogen bromide elimination took place during the rearrangements **4** to **8** and **5** to **10**, respectively, and then subsequent brominations **8** to **7** and **10** to **9** completed the reaction paths. The regiospecificity in the final bromination (at C-5) can be explained by vinylogous sulfide-like π-electron shifts in appropriate transition states as shown for bromination **8** to **7** in the proposed mechanism, discussed below (Scheme 3).

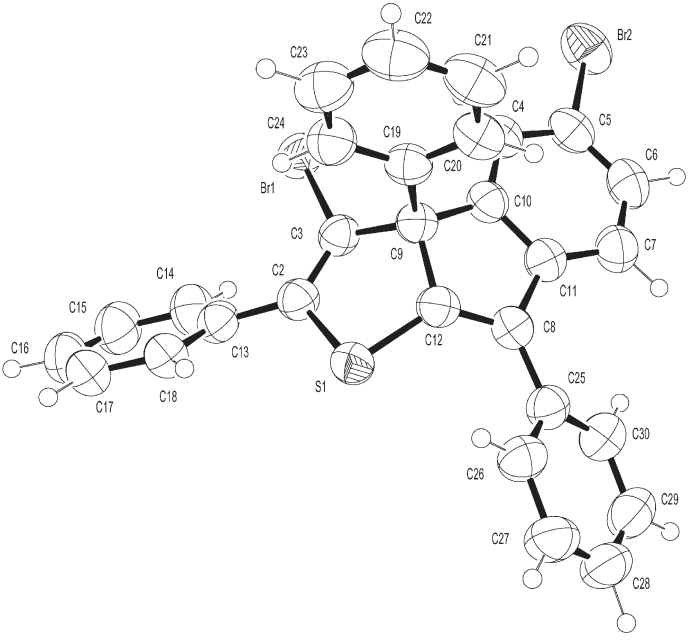
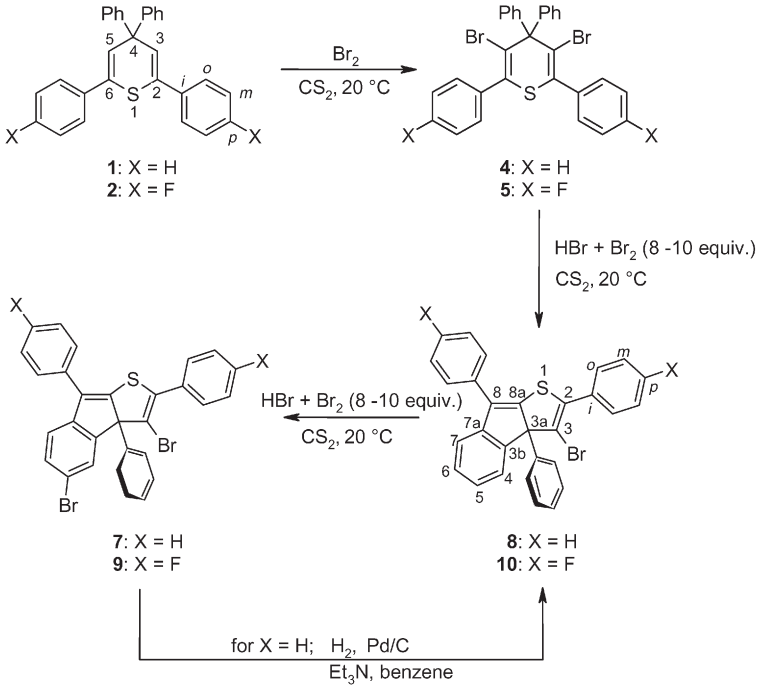
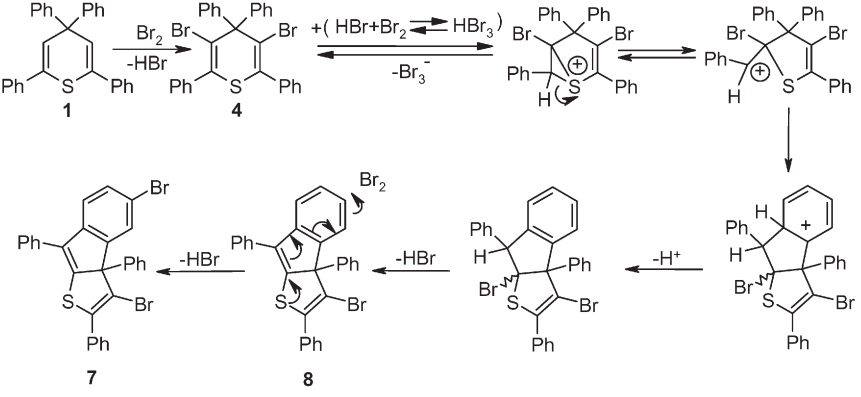


FIG. 1
ORTEP [6] view of structure of dibromo compound **7**



SCHEME 2

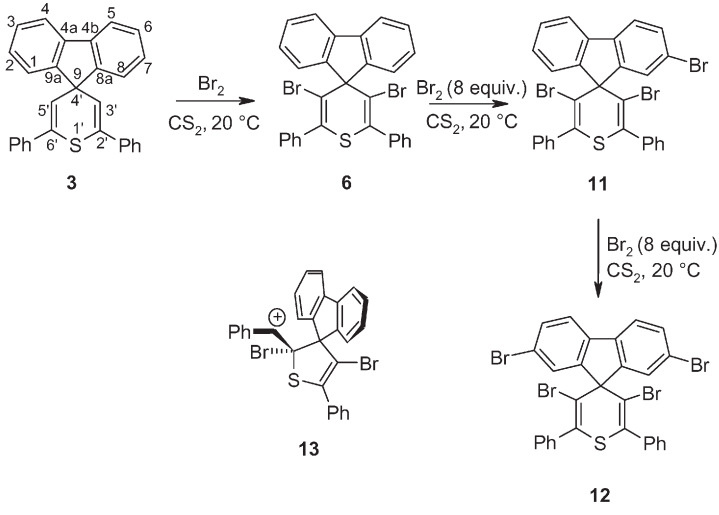
Bromine-induced isomerization of 2,4,4,6-tetraphenyl-4*H*-thiopyrans



SCHEME 3

Proposed alternative mechanism of bromine-induced isomerization

On the contrary, no rearranged products have been observed in the analogous intensive bromination of spirocyclic 4*H*-thiopyran **3**. Only 3′,5′-dibromo (**6**), 2,3′,5′-tribromo (**11**) and 2,3′,5′,7-tetrabromo (**12**), derivatives of 2′,6′-diphenylspiro[fluorene-9,4′-thiopyran] (**3**), have been detected and isolated (Scheme 4). Disubstitution of the thiopyran ring was deduced from the absence of H-3′ and H-5′ singlets in all ^{1}H NMR spectra. The coupling pattern of the fluorene protons (an ABC system) in compounds **11** and **12** was consistent either with 6- or 7-substitution. The X-ray diffraction analysis of compound **11** (Fig. 2) resolved this problem in favour of the latter alternative. Consequently, structure **12** was assigned to the tetrabromo derivative. Both compounds **6** and **12** exhibited the expected symmetry in their ^{1}H and ^{13}C NMR spectra. The regioselectivity in bromination of the fluorene moiety (2,7) might be somewhat surprising but it is apparently controlled by a biphenyl-like π-electron structure and is not an effect of the sp^3-carbon (C-9).



SCHEME 4
Bromination of 2′,6′-diphenylspiro[fluorene-9,4′-thiopyran] (**3**)

The above described heterocyclic rearrangements **4** to **7** and **5** to **9** and their absence in the case of spiroheterocycle **6** made possible to propose an alternate multistep reaction mechanism given in Scheme 3. To support the path it has been established that interaction of dry hydrogen bromide with 4*H*-thiopyran **4** does not lead to an observable change of the starting compound. Hence, bromine has to assist in the protonation of substrate **4**, per-

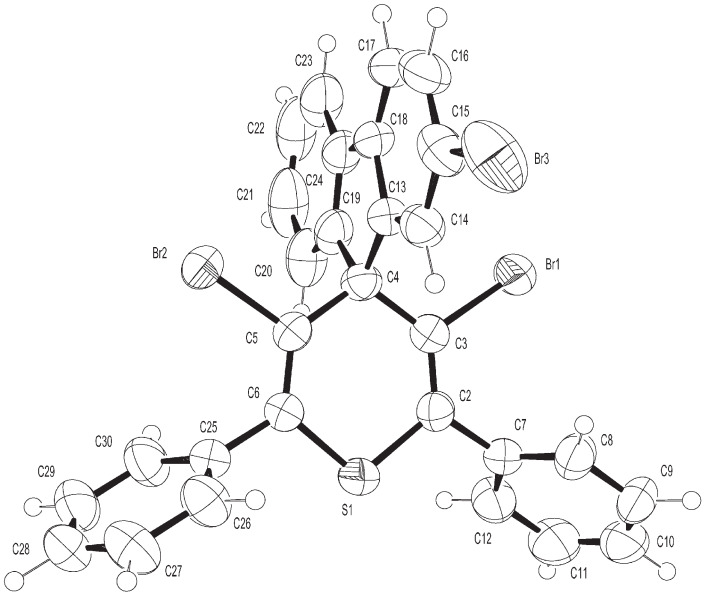


FIG. 2
ORTEP [6] view of structure of tribromospiro[fluorene-9,4′-thiopyran] **11**

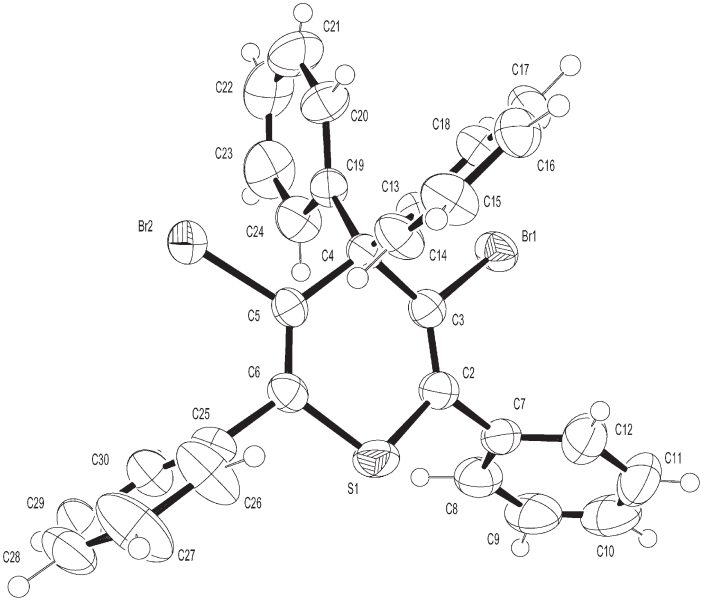


FIG. 3
ORTEP [6] view of structure of dibromothiopyran **4**

haps via an equilibrium like Br_2 + HBr $\rightleftarrows$ HBr_3, in which the resulting hydrogen tribromide[5] acts as a more powerful protonating agent in comparison with simple hydrogen bromide. A similar but less efficient influence has been detected (HPLC) in attempts to achieve the rearrangement **4** to **7** by bromination in the presence of trifluoroacetic acid.

The absence of rearranged bromination products from spiroheterocycles **3** or **6** can be rationalized. Analysis of the plausible geometry of intermediate ion **13** (Scheme 4) suggests that the side chain bearing the positive charge is not able to approach any one of the benzenoid rings because of the rigidity of the fused biphenyl-like moiety. On the other hand, a higher conformational flexibility of the phenyl groups in position 4 makes the approach possible and, consequently, the second five-membered ring closure can take place (Scheme 3).

In addition, we extend the crystal structure set of compounds **7** and **11** (Table I) with dibromo derivative **4** (Fig. 3), the structure of which is unambiguous; this compound is the intermediate of the presented isomerization. Furthermore, different photochemical behaviour of this compound in the crystalline state is remarkable[3], because the introduction of a substituent into positions 3 and 5 probably causes dramatic changes in the photochemical system. It should be noted that no X-ray data of related 3 and/or 5 (di)-substituted 2,4,4,6-tetraphenyl-4*H*-thiopyrans have been published so far.

In conclusion, the unprecedented bromine-induced isomerization of 2,4,4,6-tetraphenyl-4*H*-thiopyran into 3,5-dibromo-2,3a,8-triphenyl-3a*H*-benzo[3,4]cyclopenta[1,2-*b*]thiophene derivatives has been described together with mechanistic considerations explaining the process. This unexpected reaction is most likely catalyzed by hydrogen tribromide or perbromide, formed in the reaction of excessive bromine with hydrogen bromide from 3,5-dibromination of the starting thiopyran.

EXPERIMENTAL

Temperature data are uncorrected. Melting points were determined using a Boetius apparatus. The reactions were monitored by reverse-phase HPLC using an Ecom LCP 4000 pump on Separon SGX C18 column (3 × 150 mm, particle size 5 μm, Tessek, Czech Republic; methanol–water 9:1; UV detection at 254 nm), and TLC on Silufol UV_{254} (Kavalier Sázava, Czech Republic). Preparative column chromatography: silica gel (Aldrich 130–270 mesh), and preparative TLC (plates 20 × 20 × 0.05 cm, silica gel 5–25 μm, Aldrich; UV detection at 254 nm). Samples for elemental analysis were repeatedly crystallized, until a constant melting point was obtained and then dried in vacuo (150 Pa) over paraffin and P_4O_{10} at 110 °C or at room temperature. Starting thiopyrans **1**–**3** were prepared as described elsewhere[1c]. IR spectra (ν, cm^{-1}; $CHCl_3$) were taken on a FTIR spectrometer Nicolet 740. NMR spectra (δ, ppm; *J*, Hz) were measured on a Varian VXR-400 or Inova-400 at 400 and 100 MHz for

TABLE I
Crystal structure determination of **4**, **7**, and **11**

Compound	**4**	**7**	**11**
Formula	$C_{29}H_{20}Br_2S$	$C_{29}H_{18}Br_2S$	$C_{29}H_{17}Br_3S{\cdot}C_2H_6O$
M_r	560.35	558.34	683.27
Space group	*P*-1	$P2_1$	$P2_1/c$
a, Å	11.063(3)	7.548(3)	11.959(2)
b, Å	11.264(2)	13.129(3)	13.339(2)
c, Å	12.110(7)	11.868(3)	17.513(3)
α, °	96.29(3)		
β, °	117.12(3)	105.03(2)	92.14(1)
γ, °	110.60(2)		
Z; *V*, Å^3	2; 1189.5(10)	2; 1135.8(6)	4; 2791.7(8)
ρ_{calc}, g cm^{-3}	1.564	1.632	1.626
μ, mm	5.244	5.492	6.292
F(000)	560.0	556.0	1352.0
Crystal dimensions, mm	0.14 × 0.46 × 0.56	0.21 × 0.25 × 0.53	0.14 × 0.28 × 0.46
Diffractometer and radiation used λ, Å	Enraf–Nonius CAD4; 1.54184		
Scan technique	ω/2θ-scan		
Temperature, K	293	293	293
No. and θ range of reflections for lattice parameter refinement, °	20, 48–50	20, 38–40	20, 48–50
Range of *h*, *k*, and *l*	–11→11, –11→11, –12→12	0→9, –16→16, –14→14	–14→14, 0→16, 0→21
Total number of reflections measured 2θ range, °	5941 8–110	5040 8–150	10 688 8–136
No. of observed unique reflections	5800	4650	4563
Criterion for observed reflections	$I > 1.96\ I_o$		
Function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$		
Weighting scheme	Chebychev polynomial		
Parameters refined	370	308	335
Value of *R*, *wR*, and *S*	0.0566, 0.0677, 1.1438	0.0443, 0.0401, 1.0934	0.0736, 0.0782, 1.1092
Ratio of the maximum least-squares shift to e.s.d. in the last cycle	0.002	0.0004	0.001
Maximum and minimum heights in final Δρ map, e Å^{-3}	–1.40, 1.46	–1.34, 1.35	–0.99, 0.90

^{1}H and ^{13}C NMR, respectively, in $CDCl_3$ solutions at 25 or 30 °C. The reported assignments are based on COSY, COSY optimized for the detection of small couplings, HETCOR, HETCOR optimized for the observation of geminal and vicinal couplings, HMQC, HMBC, and 1D-TOCSY.

X-ray Structure Determinations

The crystal data and experimental conditions for compounds **4**, **7**, and **11** are summarized in Table I. Three standard reflections were monitored during data collection, showing lower than 3.5% intensity fluctuation. Decay correction and the ψ-scan[7] empirical absorption procedure were applied. The structures were solved using SIR92 [8] direct methods. The hydrogen atoms were set and kept fixed in the ideal geometry for **7** and **11** or located from Δρ-map for **4**. In this particular case the positional and U_{iso} thermal parameters of hydrogen atoms were refined. The least-squares refinements were performed in CRYSTALS [9] computing system by minimizing the function $\sum w(|F_o| - |F_c|)^2$, wherein w represents Chebyshev's polynomial weighting scheme[10]. CCDC 196172 (for **4**), 196173 (for **7**) and 196174 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

3,5-Dibromo-2,6-bis(4-fluorophenyl)-4,4-diphenyl-4*H*-thiopyran (**5**)

Bromine (0.55 g, 3.42 mmol) was added dropwise at 0 °C under stirring to a solution of thiopyran **2** (0.5 g, 1.14 mmol) in carbon disulfide (15 ml). The reaction mixture was kept at the same temperature for 1 h and then at room temperature overnight. The reaction mixture was decomposed with a saturated aqueous solution of sodium sulfite, treated with dichloromethane and the collected organic extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent in vacuo and crystallization of the residue from benzene–ethanol afforded 0.474 g (70%) of colorless crystals of dibromo derivative **5**, m.p. 216–218 °C. For $C_{29}H_{18}Br_2F_2S$ (596.3) calculated: 58.41% C, 3.04% H, 26.80% Br, 5.38% S; found: 58.01% C, 3.48% H, 26.33% Br, 5.66% S. IR: 1599. ^{1}H NMR: 7.04–7.13 (4 H, m, *o*-C_6H_4F); 7.34–7.44 (6 H, m, 4-Ph, *m*-, *p*-); 7.45–7.52 (4 H, m, 4-Ph, *o*-); 7.76–7.01 (4 H, m, *m*-C_6H_4F). ^{13}C NMR: 64.79 (C-4); 115.67 d (*m*-C_6H_4F, J(C,F) = 21.8); 116.64 (C-3, C-5); 127.40 (2 C, 4-Ph, *p*-); 127.61 (4 C, 4-Ph, *o*-); 129.38 (C-2, C-6); 130.45 (4 C, 4-Ph, *m*-); 131.06 d (4 C, *o*-C_6H_4F, J(C,F) = 8.0); 133.80 d (*i*-C_6H_4F, J(C,F) = 3.4); 141.83 (2 C, 4-Ph, *i*-); 162.75 d (*p*-C_6H_4F, J(C,F) = 249.1).

3′,5′-Dibromo-2′,6′-diphenylspiro[fluorene-9,4′-thiopyran] (**6**)

The same procedure with bromine (0.599 g, 3.75 mmol) and spirothiopyran **3** (0.5 g, 1.25 mmol) in carbon disulfide (15 ml) and recrystallization from benzene–ethanol afforded 0.454 g (71%) of colorless crystals of dibromo derivative **6**, m.p. 224–225 °C. For $C_{29}H_{18}Br_2S$ (558.3) calculated: 62.39% C, 3.25% H, 28.62% Br, 5.74% S; found: 61.32% C, 3.22% H, 28.62% Br, 6.04% S. IR: 1604, 1577. ^{1}H NMR: 7.39 (2 H, m, 2 × *p*-); 7.40 (4 H, m, 4 × *o*-); 7.44 (4 H, m, 4 × *m*-); 7.51 (2 H, m, H-3, H-6); 7.52 (2 H, m, H-2, H-7); 7.79 (2 H, m, H-1, H-8); 7.90 (2 H, m, H-4, H-5). ^{13}C NMR: 65.55 (C-9 ≡ C-4′); 112.40 (C-3′, C-5′); 119.88 (C-1,

C-8); 124.82 (C-4, C-5); 128.26 (C-2, C-7); 128.51 (C-3, C-6); 128.87 (4 × *o*-); 128.91 (2 × *p*-); 129.08 (4 × *m*-); 130.92 (C-2′, C-6′); 137.47 (2 × *i*-); 140.79 (C-4a, C-4b); 151.30 (C-8a, C-9a).

3,5-Dibromo-2,3a,8-triphenyl-3a*H*-benzo[3,4]cyclopenta[1,2-*b*]thiophene (**7**)

Bromine (6.25 g, 39.1 mmol) was added at room temperature under stirring to a solution of thiopyran **1** (2 g, 4.97 mmol) in carbon disulfide (12.5 ml) and the reaction was allowed to continue at room temperature overnight. The dichloromethane (100 ml) and saturated aqueous solution of sodium sulfite (200 ml) were added and the stirring continued for 3 h. An analogous work-up procedure to that described above and removal of the solvent afforded the crude product. The residue crystallized with petroleum–ether:dichloromethane (1:1). Recrystallization from benzene–ethanol yielded yellowish crystals (1.50 g, 54%) of the title compound **7**, m.p. 216–219 °C. For $C_{29}H_{18}Br_2S$ (558.3) calculated: 62.39% C, 3.25% H, 28.62% Br, 5.74% S; found: 62.49% C, 3.24% H, 28.29% Br, 5.49% S. IR: 1595, 1566. ^{1}H NMR: 7.36 (2 H, m, 3a-Ph, *m*-); 7.36 (1 H, m, 3a-Ph, *p*-); 7.36 (2 H, m, 3a-Ph, *o*-); 7.38 (1 H, m, 2-Ph, *p*-); 7.44 (2 H, m, 2-Ph, *m*-); 7.48 (1 H, m, 8-Ph, *p*-); 7.48 (1 H, d, *J* = 8.2, H-7); 7.52 (2 H, m, 8-Ph, *m*-); 7.52 (2 H, m, 8-Ph, *o*-); 7.56 (1 H, dd, *J* = 8.2, 1.9, H-6); 7.69 (2 H, m, 2-Ph, *o*-); 7.83 (1 H, d, *J* = 1.9, H-4). ^{13}C NMR: 77.31 (C-3a); 108.80 (C-3); 119.82 (C-5); 121.69 (C-7); 126.51 (2 C, 3a-Ph, *m*-); 127.87 (3a-Ph, *p*-); 128.17 (2 C, 8-Ph, *o*-); 128.36 (2-Ph, *p*-); 128.47 (2 C, 2-Ph, *m*-); 128.78 (C-4); 128.82 (2 C, 8-Ph, *m*-); 128.85 (8-Ph, *p*-); 128.88 (2 C, 3a-Ph, *o*-); 129.42 (2-Ph, *p*-); 131.13 (C-6); 132.45 (8-Ph, *i*-); 133.23 (2-Ph, *i*-); 138.54 (3a-Ph, *i*-); 141.28 (C-8); 143.52 (C-7a); 144.74 (C-2); 147.20 (C-8a); 150.54 (C-3b).

3-Bromo-2,3a,8-triphenyl-3a*H*-benzo[3,4]cyclopenta[1,2-*b*]thiophene (**8**)

Preparation from compound **7**. In a solution of compound **7** (1.5 g, 2.69 mmol) and triethyl amine (4 ml) in benzene (200 ml) purged with argon was suspended 0.20 g of Pd/C (10%; Aldrich) and the mixture was stirred under hydrogen at room temperature for 2 days. The resulting mixture of the starting dibromo derivative **7** and product **8** (1:1, HPLC) was filtered and evaporated in vacuo. Column chromatography (100 g, gradient elution with petroleum ether–dichloromethane 30:1–25:1) afforded 0.387 g (30%) of monobromo derivative **8** (m.p. 207–209 °C, benzene–EtOH).

Preparation from thiopyran **1**. The mother liquors after crystallization of compound **7** were combined and subjected to column chromatography (150 g, elution with petroleum ether–dichloromethane 15:1–3:1). Fraction 1 afforded 0.054 g (2%) of the compound, which was identical with 3,5-dibromo derivative **4** (m.p. 210–212 °C, heptane; lit.[3a] m.p. 211–212 °C). Fraction 2 afforded 0.018 g (0.8%) of compound **8**, which was crystallized from heptane, m.p. 206–209 °C. For $C_{29}H_{19}BrS$ (479.4) calculated: 72.80% C, 4.01% H, 16.51% Br, 6.69% S; found: 72.83% C, 4.27% H, 16.60% Br, 6.37% S. IR: 1595. ^{1}H NMR: 7.23 (1 H, ddd, *J* = 7.5, 7.5, 1.2, H-5); 7.26 (2 H, m, 3a-Ph, *m*-); 7.26 (1 H, m, 3a-Ph, *p*-); 7.27 (2 H, m, 3a-Ph, *o*-); 7.35 (1 H, m, 2-Ph, *p*-); 7.35 (2 H, m, 2-Ph, *m*-); 7.37 (1 H, m, 8-Ph, *p*-); 7.38 (1 H, ddd, *J* = 7.7, 7.5, 1.3, H-6); 7.45 (2 H, m, 8-Ph, *m*-); 7.50 (2 H, m, 8-Ph, *o*-); 7.58 (1 H, ddd, *J* = 7.7, 1.2, 0.5, H-7); 7.62 (2 H, m, 2-Ph, *o*-); 7.66 (1 H, ddd, *J* = 7.5, 1.3, 0.5, H-4). ^{13}C NMR: 77.47 (C-3a); 109.60 (C-3); 120.67 (C-7); 125.61 (C-4); 125.93 (C-5); 126.60 (2 C, 3a-Ph, *m*-); 127.60 (3a-Ph, *p*-); 128.06 (8-Ph, *p*-); 128.28 (2 C, 8-Ph, *o*-); 128.39 (2 C, 2-Ph, *o*-); 128.41 (2 C, 2-Ph, *m*-); 128.62 (C-6); 128.71 (4 C, 3a-Ph, *o*-; 8-Ph, *m*-); 129.26 (2-Ph, *p*-); 132.93 (8-Ph, *i*-); 133.46 (2-Ph, *i*-); 139.31 (3a-Ph, *i*-); 142.11 (C-8); 144.51 (C-2); 146.69 (C-8a); 148.73 (C-3b).

Bromo Derivatives of 2′,6′-Diphenylspiro[fluorene-9,4′-thiopyran] **6**, **11**, and **12**

Bromine (3.13 g, 19.6 mmol) was added at room temperature under stirring to a solution of spirothiopyran **3** (1 g, 2.50 mmol) in carbon disulfide (6 ml), the reaction was allowed to continue at room temperature overnight. The same work-up procedure as in the case of compound **7** afforded a mixture, the half of which was subjected to column chromatography on silica gel (200 g, cyclohexane–chloroform 8:1).

2,3′,5′,7-Tetrabromo-2′,6′-diphenylspiro[fluorene-9,4′-thiopyran] (**12**). Fraction 1 afforded 0.167 g (9.3%) of compound **12**, which was recrystallized from ethanol–cyclohexane, m.p. 284–286 °C (subl.). For $C_{29}H_{16}Br_4S$ (716.1) calculated: 48.64% C, 2.25% H, 44.63% Br, 4.48% S; found: 48.29% C, 2.54% H, 44.54% Br, 4.42% S. IR: 1599, 1576. ^{1}H NMR: 7.39 (2 H, m, 2 × *p*-); 7.42 (4 H, 4 × *o*-); 7.43 (4 H, 4 × *m*-); 7.57 (2 H, d, *J* = 8.1, H-4, H-5); 7.62 (2 H, dd, *J* = 8.1, 1.8, H-3, H-6); 7.94 (2 H, d, *J* = 1.8, H-1, H-8). ^{13}C NMR: 65.75 (C-4′); 110.48 (C-3′, C-5′); 121.30 (C-4, C-5); 122.40 (C-2, C-7); 128.05 (C-1, C-8); 128.61 (4 × *o*-); 129.02 (4 × *m*-); 129.13 (2 × *p*-); 132.12 (C-2′, C-6′); 132.35 (C-3, C-6); 136.95 (C-4a, C-4b); 138.82 (2 × *i*-); 152.85 (C-8a, C-9a).

2,3′,5′-Tribromo-2′,6′-diphenylspiro[fluorene-9,4′-thiopyran] (**11**). Fraction 2 afforded 0.502 g (32%) of compound **11**, which was recrystallized from ethanol–cyclohexane, m.p. 233–235 °C. For $C_{29}H_{17}Br_3S$ (637.2) calculated: 54.66% C, 2.69% H, 37.62% Br, 5.03% S; found: 54.08% C, 2.84% H, 37.53% Br, 5.10% S. IR: 1609, 1577. ^{1}H NMR: 7.39 (2 H, m, 2 × *p*-); 7.42 (4 H, m, 4 × *o*-); 7.46 (4 H, m, 4 × *m*-); 7.52 (1 H, m, H-7); 7.54 (1 H, m, H-6); 7.63 (1 H, d, *J* = 8.1, H-4); 7.65 (1 H, dd, *J* = 8.1, 1.4, H-3); 7.75 (1 H, m, H-8); 7.88 (1 H, m, H-5); 8.00 (1 H, d, *J* = 1.4, H-1). ^{13}C NMR: 65.66 (C-4′); 111.43 (C-3′, C-5′); 119.93 (C-8); 121.25 (C-4); 121.90 (C-2); 124.78 (C-4); 128.05 (C-1); 128.55 (4 × *o*-); 128.70 (C-7); 128.98 (2 × *p*-); 129.03 (4 × *m*-); 129.09 (C-6); 131.50 (C-2′, C-6′); 132.12 (C-3); 137.19 (2 × *i*-); 139.66 (C-4b); 139.91 (C-4a); 151.11 (C-8a); 153.04 (C-9a).

3′,5′-Dibromo-2′,6′-diphenylspiro[fluorene-9,4′-thiopyran] (**6**) Fraction 3 afforded 0.102 g (7.3%) of compound, recrystallized from benzene–ethanol, m.p. 223–225 °C, which was identical with compound **6**.

3,5-Dibromo-2,8-bis(4-fluorophenyl)-3a-phenyl-3a*H*-benzo[3,4]cyclopenta-[1,2-*b*]thiophene (**9**)

Bromine (3.64 g, 22.8 mmol) was added at room temperature under stirring to a solution of thiopyran **2** (1 g, 2.28 mmol) in carbon disulfide (2.5 ml) and the reaction was allowed to continue at room temperature overnight. The same work-up as in the case of compound **7** and recrystallization of the crude product from benzene–ethanol yielded yellowish crystals of **9** (0.908 g, 67%), m.p. 215–217 °C. For $C_{29}H_{16}Br_2F_2S$ (594.3) calculated: 58.61% C, 2.71% H, 26.89% Br, 5.39% S; found: 58.61% C, 3.25% H, 26.40% Br, 5.37% S. IR: 1600, 1585. ^{1}H NMR: 7.12 (2 H, AA′BB′X, $\sum J$ = 8.9, $J_{H,F}$ = 8.6, 2-Ph, *m*-); 7.20 (2 H, AA′BB′X, $\sum J$ = 8.9, $J_{H,F}$ = 8.6, 8-Ph, *m*-); 7.35 (2 H, m, 3a-Ph, *m*-); 7.35 (1 H, m, 3a-Ph, *p*-); 7.36 (2 H, m, 3a-Ph, *o*-); 7.43 (1 H, d, *J* = 8.2, H-7); 7.48 (2 H, AA′BB′X, $\sum J$ = 8.9, $J_{H,F}$ = 5.3, 2-Ph, *o*-); 7.58 (1 H, dd, *J* = 8.2, 1.9, H-6); 7.66 (2 H, AA′BB′X, $\sum J$ = 8.9, $J_{H,F}$ = 5.3, 2-Ph, *o*-); 7.85 (1 H, d, *J* = 1.9, H-4). ^{13}C NMR: 77.26 (C-3a); 109.22 (C-3); 115.69 d (2-Ph, 2 × *m*-, $J_{C,F}$ = 30.9); 115.90 d (8-Ph, 2 × *m*-, $J_{C,F}$ = 30.9); 120.04 (C-5); 121.50 (C-7); 126.39 (3a-Ph, 2 × *m*-); 127.94 (3a-Ph, *p*-); 128.50 d (8-Ph, *i*-, $J_{C,F}$ = 3.0); 128.87 (C-4); 128.94 (3a-Ph, 2 × *o*-); 129.21 d (2-Ph, *i*-, $J_{C,F}$ = 3.0), 129.93 d (3a-Ph, 2 × *o*-, $J_{C,F}$ = 8.1); 130.45 d (2-Ph, 2 × *o*-, $J_{C,F}$ = 8.4); 131.24 (C-6);

138.33 (3a-Ph, *i*-); 140.52 (C-8); 143.27 (C-7a); 143.47 (C-2); 146.70 (C-8a); 150.38 (C-3b); 162.93 d (8-Ph, *p*-, $J_{C,F}$ = 249.5); 162.98 d (2-Ph, *p*-, $J_{C,F}$ = 250.8).

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