SYNTHESIS OF SOME NEW FUNCTIONALIZED 2,4,4,6-TETRAPHENYL-4H-THIOPYRANS AND STUDY ON THEIR PHOTOCOLOURATION

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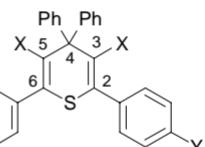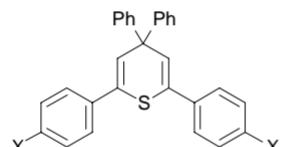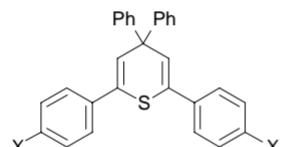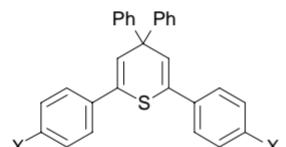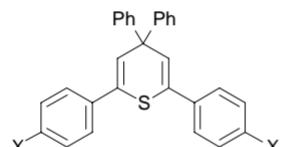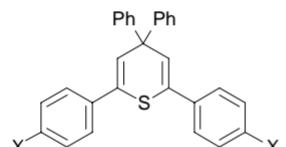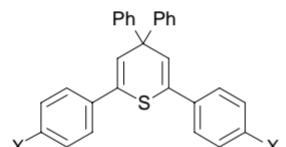
A series of nineteen new 2,4,4,6-tetraphenyl-4H-thiopyrans both symmetrically and asymmetrically functionalized in the 3- and 5-positions of the 4H-thiopyran ring (–Br, –NO₂, –CN) and/or in the 4-positions of the 2- and 6-phenyl groups (–Br, –CN, –OMe, –CO–Ph, –COCF₃, –CO₂H) was prepared and the influence of the substituents on their photocolouration was followed. The title compounds were prepared by substitution reactions of the parent thiopyrans or by cyclization of suitably substituted 1,3,3,5-tetraarylpentane-1,5-diones. The substances lacking the 3,5-substituents exhibited blue or green UV-photocolouration while the 3- and/or 5-substituted species did not. Typical bleaching process for a selected compound is analyzed in terms of dispersive first-order kinetics.
**Key words:** Thiopyrans; Cyanodebromination; Lithiodebromination; Photocolouration; Hypervalent structures; Photochromism; Photochemistry.

The photocolouration of 2,4,4,6-tetraphenyl-4H-thiopyrans[1] seems to be of general interest because their hypervalent photoisomers are proposed[2] to be formed during the process. From the previous solid state investigations[2] follows that the colouration caused by UV/VIS-illumination is only occuring on surface crystal layers with little molecular motion, the packing of the molecules has negligible effects and the observed electronic absorption spectra can be satisfactory interpreted using the CNDO/S-CI quantum chemical calculations of the isolated molecules[2]. Although the unusual photochemical behaviour has been demonstrated on several examples[1], a limited knowledge on a preparative introduction of additional substituents and their effects on the 4H-thiopyran system may be extracted from the published experimental data[3]. It appears that the heterocyclic system exhibits donating π-electron properties with the most reactive 3- and 5-positions towards electrophilic agents like chlorine[4], bromine[4a] and nitric acid[4a] allowing to obtain appropriate 3,5-disubstituted products. On the other hand, no transformations of the substances based on any various substituent displacements have yet

been reported. Hence, the aim of this paper is to investigate the preparation of some 2,4,4,6-tetraphenyl-4H-thiopyran derivatives substituted in the 3,5-positions of the heterocyclic ring and/or in the *para*-positions of the 2- and 6-phenyl groups. The strategy of the presented syntheses starting from the earlier described[4a] 3,5-dibromo-2,4,4,6-tetraphenyl-4H-thiopyran (**1**) and 2,6-bis(4-bromophenyl)-4,4-diphenyl-4H-thiopyran (**2**) is based on successive (i) bromodeprotonation with bromine, (ii) cyanodebromination of the bromo derivatives with copper(I) cyanide and (iii) lithiodebromination with butyllithium and subsequent displacement of the metal substituents by acyl groups. Attempts have been also made to convert the cyano groups to benzoyl and carboxy functions.


	1	**3**	**5**	**8**	**9**	**10**
X	Br	H	CN	Br	Br	CN
Y	H	H	H	Br	CN	CN

	2	**6**	**15**	**16**	**17**	**18**	**30**
X	Br	CN	Li	COCF$_3$	COPh	CO$_2$H	OMe

	4	**13**
X	Br	NO$_2$
Y	H	Br

	7	**23**	**24**	**25**	**26**	**27**
X	Br	Br	CN	CONH$_2$	COCF$_3$	OMe
Y	CN	OMe	OMe	OMe	OMe	H

	11	**12**	**14**
X	Br	CN	Br
Y	Br	CN	CN

	19	**20**	**21**	**22**
X	H	Br	OMe	Br
Y	H	Br	OMe	OMe

The 3,5-dibromo derivative **1** was prepared from the parent 2,4,4,6-tetraphenyl-4*H*-thiopyran (**3**) by a standard procedure[4a] using the Br$_2$/**3** ratio 2 : 1 in carbon disulfide solution under mild conditions while intermediate 3-bromo-2,4,4,6-tetraphenyl-4*H*-thiopyran (**4**) was isolated when only the ratio Br$_2$/**3** 1.3 : 1 in a more diluted solution was used. Application of the standard method[5] making use of copper(I) cyanide in DMF at elevated temperature to 3,5-dibromo derivative **1** gave expected 3,5-dicyano-2,4,4,6-tetraphenyl-4*H*-thiopyran (**5**) in 87% yield. The same procedure with 2,6-bis(4-bromophenyl) derivative **2** led to a mixture of major (40%) 2,6-bis(4-cyanophenyl)-4,4-diphenyl-4*H*-thiopyran (**6**) and minor (1.8%) asymmetrically disubstituted intermediate **7**.

To obtain tetrasubstituted derivatives of the parent 4*H*-thiopyran **3**, brominations of dibromo derivative **2** and dicyano derivative **6** have been attempted. In fact, the expected 3,5-dibromo-2,6-bis(4-bromophenyl)-4,4-diphenyl-4*H*-thiopyran (**8**) and 3,5-dibromo-2,6-bis(4-cyanophenyl)-4,4-diphenyl-4*H*-thiopyran (**9**) were prepared in 78 and 84% yields, respectively. All attempts at the cyanodebromination of compounds **8** and **9** afforded complex reaction mixtures from which only low preparative yields (1.7 and 6.4%, respectively) of 3,5-dicyano-2,6-bis(4-cyanophenyl)-4,4-diphenyl-4*H*-thiopyran (**10**) could be obtained.

An alternative approach to tetrasubstituted derivatives of the parent 4*H*-thiopyran **3** has utilized the 3,5-nitration[4a] of the heterocyclic system. Thus, 2,6-bis(4-bromophenyl)-3,5-dinitro-4,4-diphenyl-4*H*-thiopyran (**11**) was prepared by the reaction of compound **2** with 100% HNO$_3$ in chloroform. It may be noted that a change of the standard procedure[4a] with compound **2** using a large excess of nitric acid–acetic anhydride reagent led only to 3-mononitro derivative **13**. Subsequent cyanodebromination of 3,5-dinitro derivative **11** afforded a mixture from which major (42%) dicyano compound **12** and the corresponding minor (4.5%) intermediate **14** were isolated.

An additional approach to attach carbonyl-like substituents to the 2,6-diphenyl groups has been investigated. Thus, 2,6-bis(4-lithiophenyl)-4,4-diphenyl-4*H*-thiopyran (**15**) was generated *in situ* from dibromo derivative **2** and butyllithium by the recommended[6] procedure in tetrahydrofuran at –78 °C, and then converted with ethyl trifluoroacetate to 4,4-diphenyl-2,6-bis(4-trifluoroacetylphenyl)-4*H*-thiopyran (**16**) which was then isolated in 45% yield. Further experiments have been focused on functional transformations of the *para*-cyano groups in the substance **6**. The reaction of the 4*H*-thiopyran **6** with phenyllithium yielded 56% of 2,6-bis(4-benzoylphenyl)-4,4-diphenyl-4*H*-thiopyran (**17**) while dicarboxylic acid **18** was isolated in 65% yield after the reaction of **6** with potassium hydroxide in diethylene glycol followed by acidification of the reaction mixture. The prepared compounds **16**, **17** and **18** are the first examples of the sunlight sensitive 2,4,4,6-tetraaryl-4*H*-thiopyrans containing carbonyl functionality.

It has been widely documented[1c,7] that the reaction of sodium amide with any acetophenone–benzophenone mixture leads to 1,3,3,5-tetraphenyl-1,5-pentadione (**19**) (Scheme 1, X = Y = H) which can be easily heterocyclized to 4*H*-thiopyran **3** and

analogous procedure with 4-bromoacetophenone (X = Y = 4-Br) gave[7a,7b] corresponding 2,6-bis(4-bromophenyl) derivative **2**. Using a 1 : 1 ratio of 4-bromo- and 4-methoxy-acetophenones (X = 4-Br, Y = 4-OMe) a complex mixture containing expected 1,5-diketones **20**, **21** and **22** (1 : 1 : 2) was obtained, out of which the asymmetrically substituted 1-(4-bromophenyl)-5-(4-methoxyphenyl)-3,3-diphenylpenta-1,5-dione (**22**) was chromatographically isolated in 9% yield. Its heterocyclization with P_4S_{10} in xylene by the general procedure[1c] afforded the expected 2-(4-bromophenyl)-6-(4-methoxyphenyl)-4,4-diphenyl-4H-thiopyran (**23**) in 73% yield. Subsequent cyanodebromination of thiopyran **23** with copper(I) cyanide led to the expected major 2-(4-cyanophenyl) derivative **24** (59%) in addition to minor carboxamide **25** (5%) after a preparative column chromatography. Consequently, low yields of multiple-step cyanodebrominations as well as adverse effects of prolonged reaction times might be explained by the formation of analogous side products. Using the above-mentioned reactions with butyllithium and ethyl trifluoroacetate for the preparation of **16**, the asymmetrically substituted 4H-thiopyran **23** was finally converted to expected 4-trifluoro-acetyl derivative **26** accompanied by the by-product **27**. It may be noted that all attempts at an analogous reaction of diketone **20** (refs[7a,7b]) with copper(I) cyanide led to complex mixtures of hardly isolable products.

The structure of all new compounds (Table I) was confirmed by standard IR and NMR techniques. The presence of the 4H-thiopyran ring is associated with the occurrence of IR absorption bands in the region 1 583–1 614 cm^{-1}, in addition to easily identifiable functional group characteristic bands (Table I), for example two different CN stretching modes 2 218 and 2 236 cm^{-1} of tetracyano derivative **10**. ^{1}H and ^{13}C NMR signals (Tables II and III) were assigned *per analogia* using tabulated increments and considering available data[1c,4a]. In the ^{1}H NMR spectra of asymmetrically substituted derivatives **7** and **23–27** two doublets caused by about a 1.1 Hz *meta*-coupling were observed and assigned to H-3 and H-5 protons. Similarly, *para*-substituted phenyl moieties in the 2- and 6-positions were recognized by the presence of typical AA′BB′ spin patterns in the ^{1}H NMR spectra of compounds **6–14**, **16–18** and **22–27**.

Mass spectra of compounds **7**, **9–11**, **16** and **24–27** were also investigated (Table IV). The abundance of molecular ions (Table V) has been found to be strongly dependent on the 3,5-substitution patterns. Thus, for 3,5-unsubstituted compounds **7**, **16**, **24–27** as
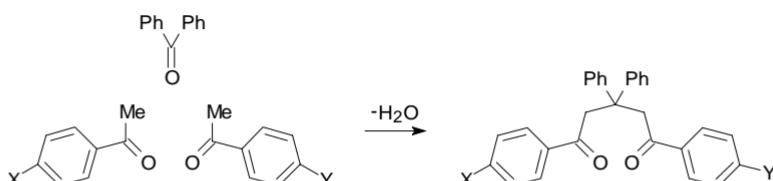
SCHEME 1

TABLE I
Characteristics of new 4*H*-thiopyrans

Compound	M.p., °C Solvent	Formula M.w.	Calculated/Found						IR spectrum (CHCl$_3$)
			% C	% H	% Br	% N	% S		
4	150–151 C_7H_{16}	$C_{29}H_{21}BrS$ 481.4	72.35 72.28	4.40 4.68	16.60 16.53	–	6.66 6.83		1 590, 1 577
5	203–205 C_7H_{16}–C_6H_6	$C_{31}H_{20}N_2S$ 452.6	82.27 82.26	4.45 4.54	–	6.19 6.05	7.08 7.01		2 214^a, 1 592, 1 575
6	238–240 MeNO$_2$	$C_{31}H_{20}N_2S$ 452.6	82.27 82.18	4.45 4.49	–	6.19 6.21	7.08 6.95		2 200^a, 1 603, 1 492
7	129–131 EtOH–Et$_2$O	$C_{30}H_{20}BrNS^b$ 506.5	71.15 71.21	3.98 3.98	15.78 –	2.77 2.65	6.33 –		2 231^a, 1 605, 1 486
8	205–207 EtOH–MePh	$C_{29}H_{18}Br_4S$ 718.1	48.51 48.47	2.52 2.76	44.51 44.07	–	4.46 4.38		1 584, 1 484
9	256–258 EtOH–CH$_3$COCH$_3$	$C_{31}H_{18}Br_2N_2S^b$ 610.4	61.00 60.85	2.97 3.37	26.18 26.23	4.59 4.37	5.25 5.32		2 233^a, 1 606, 1 497, 1 570
10	312–315 EtOH–CH$_3$COCH$_3$	$C_{33}H_{18}N_4S^b$ 502.5	78.86 78.72	3.61 4.08	–	11.15 11.01	6.38 6.29		2 236^a, 2 218^a, 1 601, 1 570
11	264–267^c C_7H_{16}–MePh–CH$_2$Cl$_2$	$C_{29}H_{18}Br_2N_2O_4S^b$ 650.3	53.56 53.41	2.79 3.00	24.57 24.70	4.31 4.26	4.93 4.91		1 614, 1 581, 1 536^d, 1 345^d
12	293–295^c C_7H_{16}–C_6H_6–EtOH	$C_{31}H_{18}N_4O_4S$ 542.6	68.62 68.73	3.34 3.29	–	10.33 10.27	5.91 5.90		2 234^a, 1 607, 1 538^d, 1 497, 1 344^d
13	182–184^c C_7H_{16}	$C_{29}H_{19}Br_2NO_2S$ 605.3	57.54 57.81	3.16 3.45	26.40 26.49	2.31 2.32	5.30 5.48		1 584, 1 528^d, 1 485, 1 348^d

TABLE I
(*Continued*)

Compound	M.p., °C Solvent	Formula M.w.	Calculated/Found					IR spectrum (CHCl₃)
			% C	% H	% Br	% N	% S	
14	286–288[c] C₇H₁₆–CH₂Cl₂	C₃₀H₁₈BrN₃O₄S 596.4	60.41 60.12	3.04 3.00	13.40 13.06	7.05 7.26	5.38 5.69	2 234[a], 1 583, 1 536[d], 1 495, 1 344[d]
16	170–171 MeCN	C₃₃H₂₀F₆O₂S[b] 594.6	66.66 66.62	3.39 3.54	– –	– –	5.39 5.64	1 718[e], 1 608, 1 491
17	183–185 EtOH–C₆H₆	C₄₃H₃₀O₂S 610.8	84.56 84.52	4.95 5.21	– –	– –	5.25 5.33	1 658[e], 1 602, 1 490
18	270–310[c] CH₃COOH	C₃₁H₂₂O₄S 490.6	75.90 76.03	4.52 4.51	– –	– –	6.54 6.33	2 540[f], 1 687[e], 1 605, 1 563
23	172–174 EtOH–C₆H₆	C₃₀H₂₃BrOS 511.5	70.45 70.74	4.53 4.80	15.62 15.45	– –	6.27 6.50	1 606, 1 510
24	166–168 EtOH–CH₃COCH₃	C₃₁H₂₃NOS[b] 457.6	81.37 81.46	5.07 5.35	– –	3.06 3.02	7.01 7.10	2 231[a], 1 606, 1 511
25	215–217 MeCN	C₃₁H₂₅NO₂S[b] 475.6	78.29 77.30	5.30 5.55	– –	2.95 2.83	6.74 –	3 532[g], 3415[g], 1 677[e], 1 608, 1 510
26	154–156 MeCN	C₃₂H₂₃F₃O₂S[b] 528.6	72.71 72.52	4.39 4.67	– –	– –	6.07 6.07	1 717[e], 1 604, 1 510
27	177–179 EtOH–C₆H₆	C₃₀H₂₄OS[b] 432.6	83.30 83.35	5.59 5.83	– –	– –	7.41 7.63	1 606, 1 509

[a] ν(CN); [b] see also Table V; [c] decomposition; [d] ν(NO₂); [e] ν(CO); [f] ν(OH), KBr technique; [g] ν(NH₂).

^{1}H NMR data of new 4H-thiopyrans

Compound[a]	δ (multiplicity, intensity, J in Hz)					
	H-3 \ H-5	H-2 (o) \ H-6 (o)	H-2 (m) \ H-6 (m)	H-4 (o)	H-4 (p) \ CH$_3$	H-4 (m)
4	6.22 \ s, 1 H	7.29–7.58[b] \ m, 20 H, +H-2(p)				
5	–	7.39–7.57[b] \ m, 16 H, +H-2 (p)		7.63 \ m, 4 H	7.39–7.57[b]	
6	6.37 \ s, 2 H	7.69[c] \ m, 8 H		7.25–7.33[b] \ m, 6 H		7.40 \ m, 4 H
7	6.23 \ d, 1 H, 1.3 \ 6.34 \ d, 1 H, 1.3	7.51 \ d, 2 H, 8.5 \ 7.69[c] \ d, 2 H, 8.5	7.45 \ d, 2 H, 8.5 \ 7.67[c] \ d, 2 H, 8.5	7.28[c] \ m, 4 H	7.25[c] \ m, 2 H	7.37 \ m, 4 H
8	–	7.52[c] \ d, 4 H, 8.4	7.25 \ d, 4 H, 8.4	7.74 \ m, 4 H	7.39 \ m, 2 H	7.47[c] \ m, 4 H
9	–	7.71[c] \ d, 4 H, 7.2	7.67[c] \ d, 4 H, 7.2		7.36–7.52[b] \ m, 10 H	
10	–	7.80 \ d, 4 H, 8.2	7.72 \ d, 4 H, 8.2		7.42–7.57[b] \ m, 10 H	
11	–	7.60[c] \ d, 4 H, 8.4	7.44 \ d, 4 H, 8.5	7.60[c] \ m, 4 H	7.36–7.44[b] \ m, 6 H	
12	–	7.76 \ d, 4 H, 7.7	7.68[c] \ d, 4 H, 7.7	7.57[c] \ m, 4 H	7.27–7.44[b] \ m, 6 H	
13	6.60 \ s, 1 H	7.58 \ d, 2 H, 8.4 \ 7.51 \ d, 2 H, 8.4	7.49 \ d, 2 H, 8.4 \ 7.38[c] \ d, 2 H, 8.4	7.37[c] \ m, 4 H	7.33 \ m, 2 H	7.42 \ m, 4 H
14	–	7.62 \ d, 2 H, 8.6 \ 7.76 \ d, 2 H, 8.5	7.42[c] \ d, 2 H, 8.6 \ 7.67 \ d, 2 H, 8.5	7.56 \ m, 4 H	7.38–7.43[b,c] \ m, 6 H	
16	6.44 \ s, 2 H	7.78 \ d, 4 H, 8.3	8.10 \ d, 4 H, 8.3	7.24–7.32[b] \ m, 6 H		7.39 \ m, 4 H
17[d]	6.41 \ s, 2 H	7.73 \ d, 4 H, 8.3	7.84[c] \ d, 4 H, 8.3	7.33 \ m, 4 H	7.28 \ m, 2 H	7.39 \ m, 4 H

Table II
(*Continued*)

Compound[a]	δ (multiplicity, intensity, *J* in Hz)					
	H-3￼H-5	H-2 (*o*)￼H-6 (*o*)	H-2 (*m*)￼H-6 (*m*)	H-4 (*o*)	H-4 (*p*)￼CH_3	H-4 (*m*)
18[e]	6.61￼s, 2 H	7.78￼d, 4 H, 8.2	8.00￼d, 4 H, 8.2	7.22–7.31[b]￼m, 6 H		7.38￼m, 4 H
23	6.26￼d, 1 H, 1.6￼6.33￼d, 1 H, 1.1	7.62￼d, 2 H, 8.8￼7.55[c]￼m, 2 H	7.55[c]￼m, 2 H￼6.97￼d, 2 H, 8.8	7.37–7.47[b]￼m, 6 H	￼3.86￼s, 3 H	7.32￼m, 4 H
24	6.38￼d, 1 H, 1.1￼6.19￼d, 1 H, 1.1	7.72￼d, 2 H, 8.2￼7.55￼d, 2 H, 8.8	7.66￼d, 2 H, 8.8￼6.93￼d, 2 H, 8.8	7.25–7.34[b]￼m, 6 H	￼3.84￼s, 3 H	7.39￼m, 4 H
25[f]	6.34￼d, 1 H, 1.1￼6.16[c]￼d, 1 H, 1.1	7.82￼d, 2 H, 8.2￼7.54￼d, 2 H, 8.8	7.68￼d, 2 H, 8.8￼6.91￼d, 2 H, 8.8		7.22–7.39[b]￼m, 10 H￼3.82￼s, 3 H	
26	6.19￼d, 1 H, 1.1￼6.47￼d, 1 H, 1.1	7.56￼d, 2 H, 8.8￼7.79￼d, 2 H, 8.8	6.94￼d, 2 H, 8.8￼8.10￼d, 2 H, 8.8		7.24–7.42[b]￼m, 10 H￼3.84￼s, 3 H	
27	6.30￼d, 1 H, 1.1￼6.21￼d, 1 H, 1.1	7.59￼d, 2 H, 8.8￼7.65￼m, 2 H	6.94￼d, 2 H, 8.8￼7.39[b]	7.39[b]￼m, 11 H￼+H-6 (*p*)	7.28￼m, 2 H￼3.84￼s, 3 H	7.39[b]

[a] In the symmetrical compounds (**4–6**, **8–12**, **16–18**) H-3, H-5 and/or H-2, H-6 protons are identical; [b] unresolved multiplet; [c] overlapping signals; [d] additional signals: 7.50 m, 4 H (Ph-*m*); 7.61 m, 2 H (Ph-*p*); 7.81[c] m, 4 H (Ph-*o*); [e] measured in $(CD_3)_2SO$, 13.09 bs, 2 H (COOH); [f] 6.15[c] bs, 2 H (NH_2).

well as for 3,5-dicyano derivative **10**, intense signals corresponding to $M^{+\bullet}$ ions were observed. On the contrary, mass spectra of 3,5-dibromo derivative **9** exhibit very weak signals of $M^{+\bullet}$ ions and with 3,5-dinitro derivative **11** no molecular ions were observed at all. Also the abundance ratios $(M - X^{\bullet})^+/(M - C_6H_5^{\bullet})^+$ are strongly affected by the mentioned substituent patterns. For the 3,5-unsubstituted and 3,5-dicyano derivatives **7**, **10**, **16** and **24–27** the abundance ratios are substantially less than unity while for the 3,5-dibromo and 3,5-dinitro derivatives **9** and **11**, the values of 2.5 and 7.0, respectively, were observed. Such behaviour seems to be in agreement with previous findings[4a]. Other important fragment ions are formed by the loss of PhX(Y) and/or

TABLE III
^{13}C NMR data of new 4H-thiopyrans

Compound[a]	C-2 / C-6	C-2 (i) / C-6 (i)	C-2 (o) / C-6 (o)	C-2 (m) / C-6 (m)	C-2 (p) / C-6 (p)	C-3 / C-5	C-4	C-4 (i)	C-4 (o)	C-4 (m)	C-4 (p)	CN
4	130.28 / 131.85	136.92 / 139.23	128.46 / 126.83	129.22 / 128.62	128.77 / 128.61	116.71 / 125.20	69.30 / –	145.58 / –	128.01 / –	129.40 / –	126.42 / –	– / –
5	133.76	141.37	128.61	128.97	131.07	108.42	56.18	148.67	128.75	128.93	128.38	116.35
6	129.65	142.36	127.26	132.53	112.44	126.41	53.63	147.19	128.07	128.80	126.95	118.44
7	136.90 / 139.85	139.93 / 142.60	128.17 / 127.21	131.81 / 132.43	122.86 / 112.19	124.32 / 126.38	53.51 / –	147.50 / –	128.06 / –	128.65 / –	126.72 / –	118.50 / –
8	129.15	136.65	127.61	131.80	123.18	116.54	64.64	141.66	130.41	130.72	127.43	–
9	128.23	142.01	127.75	132.41	112.90	117.30	64.42	141.19	129.99	130.29	127.67	118.05
10	137.75	140.55	128.88	132.93	115.22	110.50	56.26	145.72	129.18	129.55	129.00	115.46; 117.47
11	130.68	138.82	129.97	132.69	125.98	145.47	59.86	137.87	128.54	128.62	128.69	–
12	137.84	135.96	129.35	133.03	115.18	146.61	59.89	137.27	128.47	128.79	128.98	117.45
13	131.38 / 132.30	136.83 / 134.82	129.92 / 128.40	132.34 / 131.95	124.95 / 123.55	143.32 / 129.59	56.03 / –	142.41 / –	128.34 / –	128.77 / –	127.62 / –	– / –
14	130.40 / 138.02	138.63 / 136.33	129.97 / 129.36	132.81 / 133.02	126.25 / 115.06	145.47 / 146.63	59.90 / –	137.59 / –	128.52 / –	128.74 / –	128.87 / –	117.54 / –

TABLE III
(*Continued*)

Compound[a]	C-2 C-6	C-2 (i) C-6 (i)	C-2 (o) C-6 (o)	C-2 (m) C-6 (m)	C-2 (p) C-6 (p)	C-3 C-5	C-4 CH_3	C-4 (i)	C-4 (o)	C-4 (m)	C-4 (p)	CN
16[b]	129.75	144.73	127.08	130.54[c]	130.49	126.77	53.64	147.12	128.05	128.75	126.90	–
17[d]	137.46	142.01	126.44	130.35	137.54	125.49	53.56	147.69	128.13	128.31	126.66	–
18[e]	129.07	141.12	126.27	129.82	130.94	125.48	52.73	147.56	127.75	128.54	126.47	–
23	131.16	138.15	128.91	132.40	123.22	125.17	54.02	149.02	128.87	129.21	127.12	–
	131.45	131.34	128.55	114.68	160.79	123.32	55.91	–	–	–	–	–
24	130.90	143.61	127.93	133.12	112.70	127.23	54.10	148.66	128.84	129.31	127.30	119.30
	131.19	131.15	128.58	114.75	160.93	123.29	55.97	–	–	–	–	–
25[f]	130.66	142.14	126.83	127.75	168.89	125.51	53.38	148.27	128.22	128.56	126.51	–
	130.79	130.64	127.93	114.04	160.18	122.65	55.30	–	–	–	–	–
26[g]	130.55	130.38	127.95	114.09	160.29	122.61	53.48	147.99	128.21	128.65	126.66	–
	129.60	145.44	127.16	130.56[h]	130.53	127.08	55.29	–	–	–	–	–
27	131.08	130.90	127.92	113.99	160.09	122.66	53.36	148.62	128.26	128.48	126.35	–
	131.42	138.62	126.70	128.64	128.59	124.05	55.27	–	–	–	–	–

[a] In the symmetrical compounds (**5, 6, 8–12, 16–18**) C-2, C-2, C-6 and C-3, C-5 carbon atoms are identical; [b] 116.62 q, $J(C,F)$ = 289.7 (CF_3); 179.78 q, $J(C,F)$ = 34.7 (CO); [c] q, $J(C,F)$ = 2.3; [d] 128.63 (Ph-*m*), 129.97 (Ph-*o*), 132.50 (Ph-*p*), 137.56 (Ph-*i*), 195.91 (CO); [e] measured in $(CD_3)_2SO$, 166.74 (COOH); [f] 177.20 ($CONH_2$); [g] 116.72 q, $J(C,F)$ = 292.0 (CF_3); 180.00 q, $J(C,F)$ = 34.9 (CO); [h] q, $J(C,F)$ = 1.7.

$C_6H_4X(Y)$ species from molecular ions of **7**, **9–11**, **16** and **24–27**. Moreover, in the mass spectra of **9** and **11** certain ions with composition of the mass $[M - (X + HX)]$, $[M - (Ph + HX)]$, $[M - (X + Ph + X)]$, $[M - (X + PhH + HX)]$, $[M - (X + X + C_6H_4Y)]$ and $[M - (X + HX + PhY)]$ are present. Several types of ions are characteristic also in the low m/z region of the mass spectra, where ions $X(Y)C_6H_4CS^+$ seem to be structurally significant. The occurrence of ions m/z 165 and 166 most probably indicates the presence of fluorene-like fragments in accordance with mass spectra of similar previously reported[4a] compounds. In the EI spectra of amide **25** the same ions predominated as they appeared in the EI spectrum of nitrile **24**, but in the FAB mass spectra no such ions were observed. This fact could be explained by the dehydration **25→24** taking place on heating of amide **25** in a direct-inlet probe during EI MS measurements.

Only 3,5-unsubstituted 4*H*-thiopyran derivatives **6**, **7**, **16–18** and **23–27** exhibit the UV/VIS-induced photocolouration (Table V) while the 3,5-substituted ones **1**, **4**, **5** and **8–14** are inactive in the followed visible spectral region. It may be noted, that a photocolouration has been recently reported[8] for 3,5-dimethyl-2,4,4,6-tetraphenyl-4*H*-thiopyran

TABLE IV
Mass spectra of selected 4*H*-thiopyrans

Compound DI temperature, °C	m/z (relative abundance, %)
7 200	507 (M[+•], 71), 505 (M[+•], 67), 430 (100), 428 (97), 405 (5), 403 (5), 350 (13), 349 (10), 348 (10), 314 (6), 272 (7), 166 (14), 154 (19), 146 (10)
9 235	612 (M[+•], 0.7), 610 (M[+•], 1.4), 608 (M[+•], 0.7), 535 (19), 533 (41), 531 (100), 529 (82), 453 (7), 451 (10), 450 (10), 449 (8), 373 (20), 371 (13), 165 (12), 146 (14)
10 275	502 (M[+•], 71), 501 (18), 425 (100), 400 (7), 317 (13), 166 (46), 165 (19), 146 (34), 121 (6), 102 (5)
11 250	606 (M[+•], 55), 604 (M[+•], 100), 602 (M[+•], 48), 575 (8), 573 (14), 558 (10), 557 (8), 479 (6), 401 (22), 399 (16), 345 (5), 321 (10), 265 (13), 201 (7), 199 (8), 165 (15)
16 170	594 (M[+•], 65), 525 (6), 517 (100), 421 (16), 420 (17), 228 (3), 175 (5), 166 (7), 165 (9)
24 230	457 (M[+•], 94), 380 (100), 337 (13), 272 (7), 228.5 (M[2+], 4), 190 (5), 166 (11), 165 (19), 151 (10), 146 (5), 121 (4)
25[a]	476 ((M + H)[+], 100), 475 (80), 398 (65)
26 170	528 (M[+•], 100), 451 (100), 408 (8), 355 (12), 354 (10), 311 (6), 191 (7), 166 (12), 165 (18), 151 (9)
27 165	432(M[+•], 84), 355 (100), 312 (13), 247 (6), 166 (7), 165 (13), 151 (7), 121 (8)

[a] FAB ionization.

but not for analogous 3,5-diphenyl derivative. Hence, it may be suggested that the photocolouration will be limited to the 4H-thiopyrans lacking at the 3- and 5-positions electron withdrawing substituents hindering a formation of the 3,5-bridge in the proposed[2b] photoisomers like **28** or **29** shown in the Scheme 2 and formed in surface layers of their crystal matrix without significant changes of molecular shapes[2a]. However, from the kinetic studies (see bellow) it follows that two types of coloured species have been formed. A recent quantum chemical study[9] on a more extended series of π-electron molecular systems containing the C=S=C moiety also supports the existence of

Ar^1 and Ar^2 : 4-X-phenyl or 4-Y-phenyl
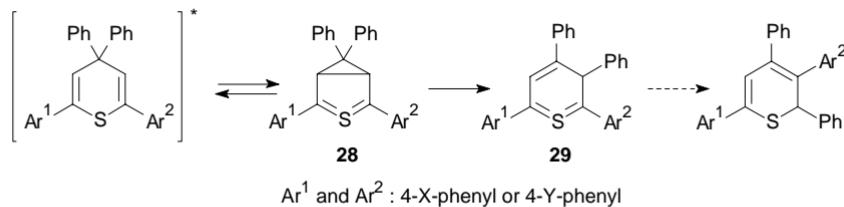
SCHEME 2

such hypervalent species. Data in Table VI suggest that the substituents X and Y affected to a certain degree the visible absorption of the coloured **28**-like photoisomers. It reveals that the strongly π-electron with-drawing groups like COCF$_3$, COPh, CO$_2$H, and partly CN, shift the maximum of the visible absorption bands to longer wave-

TABLE V

High-resolution mass spectral elemental analysis of selected 4H-thiopyrans

Compound	Found	Calculated	Elemental composition	Type of ion
7	505.0505	505.0500	$C_{30}H_{20}NS^{79}Br$	$M^{+\bullet}$
9	529.0373	529.0374	$C_{31}H_{18}N_2S^{79}Br$	$(M - Br)^+$
10	502.1241	502.1252	$C_{33}H_{18}N_4S$	$M^{+\bullet}$
11	601.9432	601.9425	$C_{29}H_{18}NO_2S^{79}Br_2$	$(M - NO_2)^+$
16	594.1077	594.1088	$C_{33}H_{20}O_2SF_6$	$M^{+\bullet}$
24	457.1508	457.1500	$C_{31}H_{23}NOS$	$M^{+\bullet}$
25	475.1613	475.1606	$C_{31}H_{25}NO_2S$	$M^{+\bullet}$
26	528.1362	528.1371	$C_{32}H_{23}O_2SF_3$	$M^{+\bullet}$
27	432.1550	432.1548	$C_{30}H_{24}OS$	$M^{+\bullet}$

lengths in comparison to earlier observed[1c] maxima of **28** out of 4*H*-thiopyrans **2** (398 and 564 nm) and **30** (394 and 600 nm).

Basic characteristics of the absorption spectra of the active substances **6**, **7**, **16–18**, **23**, **24** and **26** in chloroform show (Table VI) that, generally, four absorption peaks at wavelengths $\lambda = 234 \div 242$ nm, $252 \div 268$ nm, $277 \div 298$ nm and $312 \div 360$ nm can be observed. The first and third absorption bands are as a rule superimposed on the main

TABLE VI
UV-VIS absorption maxima of the compounds studied

Compound[b]	Starting 4*H*-thiopyran (CHCl$_3$)		28-like photoisomers (solid state)[a]		
	λ_{max}, nm[c,d]	log ε[e]	4-X	4-Y	λ_{max}, nm[d]
3	250 (270 sh)	4.47	H	H	564 s, 381
6	260 (312 m, 242 s)	4.55	CN	CN	647 s, 422
7	252 (320 w, 252 sh)	4.60	Br	CN	613 s, 410
16	292 (342 m, 252 s)	4.52	COCF$_3$	COCF$_3$	667 m, 470
17	258 (333 m, 285 s)	4.60	COPh	COPh	656 w, 407
18	268 (318 m, 242 sh)	4.51	CO$_2$H	CO$_2$H	642 s, 418
23	254 (277 sh)	4.58	Br	OMe	610 m, 392
24	256 (326 w, 281 sh)	4.57	CN	OMe	621 s, 437
26	262 (360 w, 298 sh)	4.50	COCF$_3$	OMe	672 s, 467

[a] Polycrystalline powder in MgO after 15 s irradiation with a high pressure 200 W mercury discharge lamp with an appropriate filter 230 nm < $\lambda \leq$ 350 nm; [b] before UV-illumination; [c] main maximum, satelites are given in parentheses; [d] symbols: s strong, m medium, w weak, sh shoulder; [e] ε in dm^3 mol^{-1} cm^{-1}.
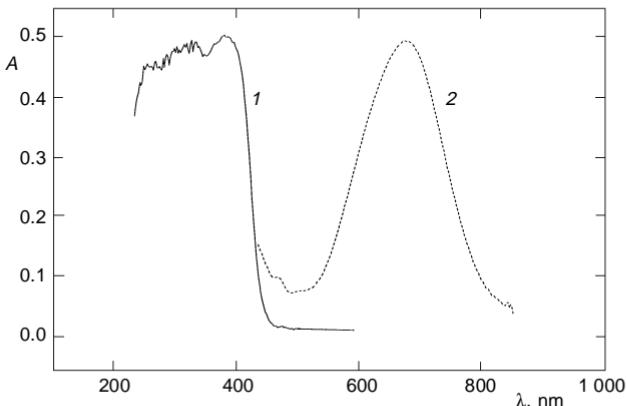

Fig. 1

UV-VIS absorption spectra of powder **26** at room temperature: *1* before UV irradiation, *2* photochromic bands after UV exposure

peak and are usually observed as main peak shoulders. The absorption spectra of the solid phase are shifted to the red (Fig. 1); the first absorption band is observed at $\lambda = 320 \div 380$ nm. Immediately after the irradiation of the substances under study with the light of $\lambda_{exc} \leq 350$ nm at room temperature, a green or blue colour was observed. The typical difussion-reflection spectrum for 4H-thiopyran **26** (X = 4-COCF$_3$, Y = 4-OMe) is given in Fig. 1; the maximum of the new absorption lies at 672 and *ca* 467 nm. As it follows from Table VI, the new absorptions are shifted to the red for all substituted substances in comparison with unsubstituted compound **3** in the solid phase. The photocolouration was also observed in solutions by flash photolysis. Here, four transient absorption bands were observed; *e.g.* for the substance **3**, the bands 310, 370, 420 and (530 ± 10) nm were detected. The ratios of absorbances of these peaks are 92 : 20 : 10 : 1. This transient absorption represents short lived species, $\tau = 180$ μs (monomolecular reaction). Evidently, the coloured species are stabilized in the solid state where two absorption bands were detected for $\lambda > 370$ nm: $\lambda_1 = 381$ nm, $\lambda_2 = 564$ nm with the ratio of absorbances 1 : 2. The alternation of the absorbance intensities for the band maxima at 381 and 564 nm (rigid phase) and 370 and 530 nm (solution) and the missing of the band at 420 nm in the rigid phase suggests that at least two types of species like **28** and **29** are responsible for the colouration process. Moreover, the dispersitivity of the bleaching process in the rigid phase, which time dependence can be expressed by a stretched exponential function

$$[M(t)]/[M(0)] = \exp\left[-(\nu t)^{\alpha}\right] , \tag{1}$$

where $0 < \alpha < 1$ measures the deviation from the our exponential behaviour, ν is the decay rate constant, $[M(t)]$ and $[M(0)]$ is the concentration of the coloured species at the time t and time $t = 0$, respectively, can follow from several facts: (i) the superposition of several exponentials of several coloured species, (ii) the broad distribution of
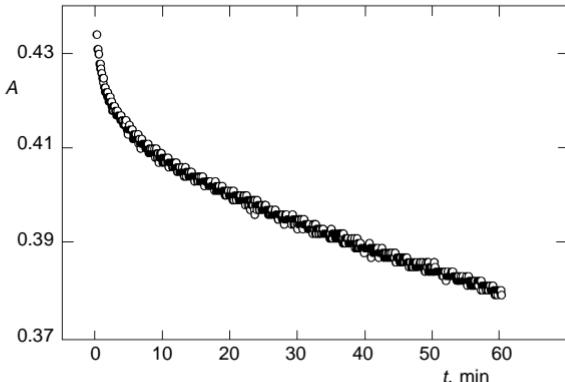

Fig. 2

Thermal bleaching of **28**-like species (polycrystalline UV-irradiated sample of 4H-thiopyran **26** mixed with MgO) at room temperature

the relaxation times and (iii) statistical distribution of thermodynamic reaction parameters, especially in polycrystalline materials.

Concerning the case (iii), the optical properties of disordered polycrystalline material must be regarded as resulting from a set of individual processes of different rates, weighted by the distribution of parameters. If the kinetics are first-order at each site, the superposition of time independent rates will cause the overall rate of the process to be time dependent. The corresponding decay low for these dispersive processes[10a] differs from the pure exponential form and follows exp $(-t^\alpha)$.

In irregular systems, such as in the polycrystalline material, activation energies and entropies of the photochromic back reaction depend on the local geometry around the reacting species, and, consequently, they are quantities with statistical variation. The thermally induced back reaction is associated with the rate constant $\nu(E)$ according to the relation

$$\nu(E) = \nu_0 \exp \left[-(E_m - E)/kT \right] , \qquad (2)$$

where ν_0 is the frequency factor and E is the energy. Since the difference between the ground state energy E and the maximum E_m of the energy barrier depends on a set of conformational parameters, each varying statistically, the most probable distribution function for $E_m - E$ was assumed[10b] to be a Gaussian function characterized by its width σ. Therefore, the time dependence of the concentration of coloured species should be the convolution of first-order decay functions reflecting the monomolecular nature of the reaction and the distribution function for the reaction rates

$$[M(t)] = \{[M(0)]/(2\pi\sigma^2)^{1/2}\} \int \exp \{-(E_0 - E)^2/2\sigma^2\} \exp \{-\nu(E)t\} \, dE . \qquad (3)$$

The experimental results in air for the substance **3** have given the following parameters at $T = 288$ K: $\alpha = 0.64$, $\sigma = 0.033$ eV, $\nu = 8.42 . 10^{-5}$ s^{-1}. The decay process was possible to describe with one stretched exponential function. The photocolouration process was found to be reversible, *i.e.* colouration with UV irradiation and thermal bleaching could be repeated many times. It could be pointed out that the bleaching in the rigid phase is much slower, several hundreds microseconds in solution. The bleaching process in the case of the substituted substances **6**, **7**, **16–18**, **23**, **24** and **26** (see Table VI) was different. Here, it was impossible to make successful fits of the decay curves by a single-stretched exponential function, but two functions had to be used. A typical example of the course of the thermal bleaching for compounds **26** is given in Fig. 2. The successful fit was obtained by two-stretched exponentials with $\alpha_1 = 0.69$ for shorter times ($t < 1.5$ min) and $\alpha_2 = 0.34$ for longer times. It means that at least two coloured species like **28** and **29** are responsible for the photocolouration process. The substitution strongly but not lucidly influences the speed of the thermal bleaching: 4*H*-thiopyrans **16**, **24** and **26** bearing the groups COCF$_3$ and OMe behave as the parent

4H-thiopyran **3**, *e.g.* the bleaching is longer than 10 h, while the substituents Br, CN, COPh, CO$_2$H and OMe in the compounds **6**, **7**, **17**, **18** and **23** make the bleaching process shorter.

EXPERIMENTAL

Temperature data are uncorrected. Melting points were determined using a Boetius apparatus. NMR spectra (δ, ppm; J, Hz) were measured on a GEMINI 300 HC instrument (deuteriochloroform solutions, TMS as internal standard) at 298 K. Homocorrelated 2D NMR experiments COSY and ROESY were used to resolve overlapping signals in ^{1}H NMR spectra (Table II). IR spectra (ν, cm^{-1}; CHCl$_3$) were taken on a FTIR spectrometer NICOLET 740. UV-VIS absorption spectra were measured in chloroform using a Hewlett–Packard 8451A recording spectrophotometer. The diffuse reflectance of polycrystalline powders were recorded by a Perkin–Elmer–Hitachi 340 instrument. Electron ionization spectra were mesured on a VG-7070E mass spectrometer with double focusation (EB geometry, ion source temperature 250 °C, ionizing electron current 50 μA, ionizing electron energy 70 eV, accelerating voltage 6 kV). Samples were introduced using a direct inlet probe and heated to lowest temperature necessary to record spectra of desired quality. Accurate mass measurements were performed by the peak matching technique at a resolving power of 7 000 (10% valley definition) with perfluorokerosene as standard and HRMS data are given in Table V. Fast atom bombardment (FAB) mass spectrum of compound **25** was recorded on the same instrument. A standard saddle field FAB gun was operated at 8 kV and 2 mA. Xenon as bombarding gas and a matrix of 3-nitrobenzyl alcohol were used. HPLC was performed on a Separon SGX C18 column (3 × 150 mm, particle size 5 μm, Tessek, Czech Republic) in the inversion phase (methanol–water 9 : 1, UV detection at 254 nm), and TLC on Silufol UV$_{254}$ (Kavalier, Czech Republic). Preparative column chromatography: silica gel (Aldrich) and preparative TLC (plates 20 × 20 × 0.05 cm, silica gel Aldrich, 5–25 μm, UV detection at 254 nm). Samples for elemental analysis were dried *in vacuo* (*ca* 150 Pa) over paraffine and P$_4$O$_{10}$ at 110 °C or at room temperature.

3-Bromo-2,4,4,6-tetraphenyl-4H-thiopyran (**4**)

2,4,4,6-Tetraphenyl-4H-thiopyran[1c] **3** (7.00 g, 17.4 mmol) was added at 0 °C to a stirred solution of bromine (3.46 g, 22.6 mmol) in carbon disulfide (910 ml). After stirring for 3 h at 0 °C and for 18 h at room temperature the reaction mixture was decomposed with a saturated aqueous solution of sodium sulfite, treated with dichloromethane and the collected organic extracts were dried with magnesium sulfate. Evaporation of the solvent *in vacuo* and crystallization of the residue afforded 7.78 g (93%) colourless crystals of monobromoderivative **4**, see Tables I–III.

Preparation of Cyano Derivatives **5–7**, **10**, **12**, **14** and **24**. General Procedure

Dry DMF (13–30 ml) was added under argon and stirring to bromo derivative **1**, **2**, **8**, **9**, **11** or **23** (10–60 mmol) and copper(I) cyanide[11] (2–25 equivalents) and the mixture was then stirred at 175–185 °C until disappearance of the starting compound (7.5–15 h). After cooling the reaction mixture was poured into saturated solution of ammonium chloride in aqueous ammonia. The resulting precipitate was filtered off, washed with water and dissolved in dichloromethane. The extract was dried with magnesium sulfate, evaporated and subjected to column chromatography (silica gel 100–250 g, eluents, see below). Crude products were purified by crystallization, see Table I, and the following yields of the products were achieved: **5** (87%, CHCl$_3$–C$_6$H$_6$ 1 : 1), **6** and **7** (40 and 1.8%, CH$_2$Cl$_2$ or CHCl$_3$), **10** (1.7 and 6.4% from compounds **8** and **9**, respectively, CH$_2$Cl$_2$–AcOEt 1 : 1 and then

preparative TLC, PE–CH$_2$Cl$_2$–AcMe 12 : 8 : 1), **14** and **12** (4.5%, PE–CH$_2$Cl$_2$ 1 : 1, 42%, PE–CH$_2$Cl$_2$ 1 : 2 and then CH$_2$Cl$_2$), and **24** and **25** (59 and 5%, PE–CH$_2$Cl$_2$ 1 : 1 and then preparative TLC, CH$_2$Cl$_2$–AcOEt 1 : 1) Individual spectral characteristics are given in Tables I–V.

3,5-Dibromo-2,6-bis(4-bromophenyl)-4,4-diphenyl-4*H*-thiopyran (**8**)

Bromine (2.3 g, 14.4 mmol) was added dropwise at 0 °C and under stirring to a solution of thio-pyran[1c] **2** (2.74 g, 4.87 mmol) in carbon disulfide (55 ml), the reaction was allowed to continue for 3 h at the same temperature and then let at room temperature overnight. The same work-up procedure as in the case of **4** yielded 2.42 g (78%) of tetrabromo derivative **8** as brownish crystals, see Tables I–III.

3,5-Dibromo-2,6-bis(4-cyanophenyl)-4,4-diphenyl-4*H*-thiopyran (**9**)

A solution of bromine (0.94 g, 7.84 mmol) in carbon disulfide (20 ml) was added under stirring at 0 °C to thiopyran **6** (0.886 g, 1.96 mmol) in CH$_2$Cl$_2$ (15 ml). The mixture was stirred at 0 °C for 3 h and at room temperature for 18 h. Then after cooling to 0 °C an additional portion of dibromine (4.07 g, 34.0 mmol) was added and the mixture was finally stirred 5 h at 0 °C. An analogous work-up as in the case of **4** led to colourless crystals (1.01 g, 84%) of 3,5-dibromo derivative **9**, see Tables I–V.

2,6-Bis(4-bromophenyl)-3,5-dinitro-4,4-diphenyl-4*H*-thiopyran (**11**)

Fuming 100% HNO$_3$ (2.43 ml, 53.4 mmol) was added at 0 °C to a stirred solution of thiopyran **2** (2.00 g, 3.57 mmol) in chloroform (15 ml) and the reaction mixture was stirred for 1 h at the same temperature. The collected organic layers obtained after treatment with water to pH 7 and an additional extraction of the aqueous phase with dichloromethane were dried with magnesium sulfate and evaporated. The reaction mixture did not contain mononitro derivative **13** and was separated by loose-layer chromatography on silica gel (70 g, petroleum ether–chloroform 1 : 1). Crystallization of the crude product afforded yellow crystals (0.724 g, 31%) of dinitrothiopyran **11**, see Tables I–V.

2,6-Bis(4-bromophenyl)-3-nitro-4,4-diphenyl-4*H*-thiopyran (**13**)

A mixture of 63% nitric acid (12.12 g, 121 mmol), thiopyran **2** (0.5 g, 0.892 mmol) and dichloro-methane (5 ml) was gradually added to stirred acetanhydride (54.19 g, 531 mmol) cooled with a salt-ice bath (–15 °C). After 23 min the reaction was quenched by pouring the mixture on ice, dichloromethane (30 ml) was added and the resulting two-phase system was worked up as in the case of **11**. Preparative TLC on silica gel (45 g, petroleum ether–dichloromethane 2 : 1) followed by crystallization yielded yellow crystals (0.150 g, 28%) of mononitro derivative **13**, see Tables I–III.

2,6-Bis(4-trifluoroacetylphenyl)-4,4-diphenyl-4*H*-thiopyran (**16**)

Thiopyran **2** (2 g, 3.56 mmol) was heated in a mild argon flow to *ca* 70 °C and after cooling to room temperature, tetrahydrofuran (50 ml) was added under argon. The solution was cooled at –78 °C in the inert atmosphere and butyllithium (4.7 ml, 8.51 mmol) in hexane (1.81 M solution) was added in portions. The resulting yellow slurry precipitate of **15** stirred for 15 min at –78 °C and then ethyl trifluoroacetate (2.12 ml, 2.53 g, 17.8 mmol) was added at once under vigorous stirring. The colour of the reaction mixture was changed from blue (several seconds) to brown and the mixture was allowed to reach room temperature (40 min). The solution was decomposed with saturated aqueous ammonium chloride (200 ml) and shaken up with diluted hydrochloric acid, treated with diethyl ether (2 × 50 ml), combined organic layers were washed with saturated aqueous sodium hydrogencarbonate solution, dried with magnesium sulfate and evaporated. Column chromatography on silica gel (200 g,

petroleum ether–dichloromethane 1 : 1) and repeated crystallization afforded colourless needles, (0.957 g, 45%) of thiopyran **16**, see Tables I–V.

2,6-Bis(4-benzoylphenyl)-4,4-diphenyl-4H-thiopyran (**17**)

The reaction of thiopyran **6** (0.485 g, 1.10 mmol) in diethyl ether (15 ml) with phenyllithium in diethyl ether (1.18 M solution, 3.2 ml, 3.78 mmol) under vigorous stirring at 0 °C was performed in the same manner as in the above-mentioned case but only for 1 h at 0 °C and the reaction mixture was allowed to stand overnight at ambient temperature. The resulting solution was poured into aqueous 5% NaOH (200 ml), extracted with dichloromethane, washed with water, dried with magnesium sulfate and evaporated. Column chromatography on silica gel (50 g, benzene) and crystallization resulted in yellowish crystals (0.373 g, 56%) of dibenzoyl derivative **17**, see Tables I–III.

2,6-Bis(4-carboxyphenyl)-4,4-diphenyl-4H-thiopyran (**18**)

Thiopyran **6** (1 g, 2.21 mmol) and potassium hydroxide (0.75 g, 13.7 mmol) in diethylene glycol (20 ml) were stirred and heated at 180 °C for 2 h. The resulting mixture was poured onto water (200 ml), extracted with chloroform (50 ml) and diethyl ether (2 × 50 ml). The aqueous layer was then heated to 50 °C to remove residual diethyl ether and acidified with diluted sulfuric acid. After recooling, the precipitate of crude product was collected on a sintered-glass filter, thoroughly washed with water, recrystallized and the crystals washed with a small amount of dichloromethane. Dicarboxylic acid **18** (0.704 g, 65%) was obtained as finely crystalline powder, see Tables I–III.

1-(4-Bromophenyl)-5-(4-methoxyphenyl)-3,3-diphenylpentane-1,5-dione (**22**)

A solution of benzophenone (22.5 g, 0.123 mol), 4-methoxyacetophenone (15 g, 0.1 mol) and 4-bromo-acetophenone (20 g, 0.1 mol) in diethyl ether (50 ml) was added dropwise to a stirred suspension of sodium amide (14.5 g, 0.35 mol) in diethyl ether (100 ml) cooled in ice-water bath. The reaction mixture was stirred for 2 h at room temperature and allowed to stay overnight. After 1 h heating on water bath it was carefully decomposed by water (200 ml) and extracted with benzene. Collected organic layers were washed with water, diluted sulfuric acid, repeatedly with water and after drying with magnesium sulfate evaporated *in vacuo*. The residue was subjected to water steam distillation (2 h), extracted with benzene and organic extracts were worked up as above. The crude residue was subjected to column chromatography on silica gel (600 g, 7 × 35 cm) with cyclohexane and then with benzene. Fractions containing diketone **22** (TLC, R_F = 0.4, benzene) were evaporated and let to crystallize from methanol (3 ml) and acetonitrile (0.5 ml) under cooling. Recrystallization from ethanol–benzene and then from xylene yielded colourless crystals (4.75 g, 9%) of diketone **22**, m.p. 131–132 °C. For $C_{30}H_{25}O_3Br$ (513.4) calculated: 70.18% C, 4.91% H, 15.56% Br; found: 69.92% C, 5.06% H, 15.33% Br. IR spectrum: 1 689 (C=O), 1 601, 1 585 (C=C arom.). ^{1}H NMR spectrum: 3.81 s, 3 H (OMe); 4.32 s, 2 H (H-2); 4.38 s, 2 H (H-4); 6.83 d, 2 H, J = 8.8 (m-C_6H_4OMe); 7.15 m, 2 H (p-Ph_3); 7.21–7.31 m, 8 H (o,m-Ph_3); 7.49 d, 2 H, J = 8.8 (m-C_6H_4Br); 7.69 d, 2 H, J = 8.8 (o-C_6H_4Br); 7.82 d, 2 H, J = 9.3 (o-C_6H_4OMe). ^{13}C NMR spectrum: 44.20 CH_2 (C-4); 44.83 CH_2 (C-2); 47.37 C (C-3); 55.26 CH_3 (OMe); 113.44 CH (m-C_6H_4OMe); 126.17 CH (p-Ph_3); 127.52 CH (o-Ph_3); 127.75 C (p-C_6H_4Br); 128.07 CH (m-Ph_3); 129.47 CH (o-C_6H_4Br); 130.19 CH (o-C_6H_4OMe); 131.29 C (i-C_6H_4OMe); 131.57 CH (m-C_6H_4Br); 136.84 C (i-C_6H_4Br); 147.87 C (i-Ph_3); 163.27 C (p-C_6H_4OMe); 197.69 C (C-5); 198.25 C (C-1).

2-(4-Bromophenyl)-6-(4-methoxyphenyl)-4,4-diphenyl-4*H*-thiopyran (**23**)

A mixture of diketone **22** (3 g, 5.84 mmol) and P_4S_{10} (4 g, 9.0 mmol) in xylene (50 ml) was stirred under nitrogen and heated at 135 °C and the conversion was monitored by HPLC. After 10 h another portion of P_4S_{10} (4 g, 9.0 mmol) was added and the reaction was finished after 17 h. The mixture was filterred off, evaporated *in vacuo* and the crude product was purified by column chromatography on silica gel (150 g, cyclohexane and then benzene). The product **23** was recrystallized to afford 2.19 g (73%) of colourless needles, see Tables I–III.

2-(4-Methoxyphenyl-6-(4-trifluoroacetylphenyl)-4,4-diphenyl-4*H*-thiopyran (**26**)
and 2-(4-Methoxyphenyl)-4,4,6-triphenyl-4*H*-thiopyran (**27**)

Reaction of 4*H*-thiopyran **23** (0.5 g, 0.978 mmol) with a solution of butyllithium in hexane (0.65 ml, 1.173 mmol) and ethyl trifluoroacetate (0.35 ml, 2.933 mmol) was performed in the same manner as in the case of **16**. The crude reaction mixture was separated by column chromatography on silica gel (50 g, petroleum ether–dichloromethane 1 : 1). First fractions afforded, after evaporation and crystallization, white crystals of by-product **27** (71 mg, 17%) while the following fractions gave yellow crystals of the expected product **26** (0.291 g, 56%), see Tables I–V.

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