Novel Preparation and Photochromic Properties of 2,4,4,6-Tetraaryl-4Hthiopyrans

Pavel Šebek,^a Stanislav Nešpůrek,^{b,*} Richard Hrabal,^a Mojmír Adamec^b and Josef Kuthan⁴

^a Department of Organic Chemistry and Laboratory of Nuclear Magnetic Resonance, Prague Institute of Chemical Technology, 166 28 Prague, Czechoslovakia ^b Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague, Czechoslovakia

1,3,3,5-Tetraarylpentane-1,5-diones 2 and 5 react with tetraphosphodecasulfide in xylene at elevated temperature to give the corresponding 2,4,4,6-tetraaryl-4H-thiopyrans 4 and 7. The mechanism of this transformation involves a fast initial step of dehydration of 2 and 5 to 2,4,4,6-tetraaryl-4Hpyrans 3, followed by a slower transformation to the 4H-thiopyran analogues 4. Using 2D NMR techniques, a complete assignment of the ¹H and ¹³C NMR spectra of the 1-oxide and 1,1-dioxide analogues of 4 (1, X = SO and SO_2) as well as of compounds 3c, j, l, m, 4a-m, 6 (the pyran analogue of 7) and 7 has been carried out. Compounds 4 and 7 undergo a reversible photochemical colour change after UV illumination. The maxima of the new absorption bands are situated at 540-660 nm. The non-exponential time dependence of the photodecolouration of 4a in the solid state is analysed in terms of dispersive first-order reaction kinetics. Dioxygen accelerates the decolouration process; the half-life at 299 K lies between 6600 s in air and several days in a vacuum (10⁻³ Pa). The trapping of photoproducts 10a, 10e and 11a enables us to postulate the whole photolysis sequence.

Heterocyclic compounds of general formula 1, where X = O, Sor NR, represent an interesting group of substances exhibiting photochemical colour changes. It is known that 4H-pyrans,^{1,2} 4H-thiopyrans ^{3,4} and 1,4-dihydropyridines ^{1,2,5-7} change their colour from white to red, violet or blue when illuminated with UV light, sunlight or X-rays. Similar molecular structures for the species causing this photocolouration have been considered on the basis of pure speculation^{3,4} or quantum chemical calculations.⁸ In this paper the synthesis, characterization and study of the photocolouration of 2,4,4,6-tetraaryl-4H-thiopyrans 4a-m and 7 are reported. The detailed mechanism of the photochromic behaviour is discussed with respect to model compound 4a.



b: $Ar = 4-MeOC_6H_4$, $Ar^1 = Ar^2 = Ph$ h: Ar = Ar^1 = Ph, Ar^2 = 4-CIC₆H₄ c: $Ar = 4-Bu^{1}C_{6}H_{4}$, $Ar^{1} = Ar^{2} = Ph$ i: $Ar = Ar^1 = Ph, Ar^2 = 4-BrC_6H_4$ d: $Ar = 4-MeC_6H_4$, $Ar^1 = Ar^2 = Ph$ $j_1 = Ar^2 = 4-Bu^t C_6 H_4$ **k:** Ar = Ph, $Ar^1 = Ar^2 = 4 - MeC_6H_4$ e: Ar = 4-FC₆H₄, Ar¹ = Ar² = Ph f: Ar = 4-BrC₆H₄, Ar¹ = Ar² = Ph I: g: Ar = Ar¹ = Ph, Ar² = 4-MeC₆H₄



 $Ar = Ph, Ar^{1} = Ar^{2} = 4-FC_{6}H_{4}$

Results and Discussion

Preparation of 4H-Thiopyrans 4a-m and 7.--Of the title compounds, 2,4,4,6-tetraphenyl-4H-thiopyran 4a and some of its variously substituted derivatives have been prepared previously, mostly in variable yields and in mixtures with their 2H-isomers, as products of thermal or photochemical rearrangements of the corresponding 1,2,4,6-tetraarylthiabenzenes, obtained by reaction of organolithium on organomagnesium reagents with 2,4,6-trisubstituted thiopyrylium salts.^{4,9-14} In this study 4H-thiopyrans 4a-m were prepared by employing a procedure described previously¹⁶ and based on readily available^{1,5,7,17,18} 1,3,3,5-tetraarylpentane-1,5diones 2, which, on heating with tetraphosphodecasulfide in xylene, yield the corresponding 4H-thiopyrans 4. Similarly, 1,5-dione 5⁷ was transformed to 7. An alternative heterocyclization of 2a, brought about by simultaneous treatment with hydrogen sulfide and hydrogen chloride,¹⁶ resulted in lower yields of 4a.

In the HPLC study of the time dependence of transformation 2a-4a carried out using tetraphosphodecasulfide we arrived at a remarkable finding which indicates the key intermediate of the process. Fig. 1 shows that two kinetically different stages are operative in this case. In the first stage, which is faster, the 4H-pyran 3a is formed, which, in the second, slower stage, is transformed to the 4H-thiopyran 4a. At 413-418 K the whole process $2a \rightarrow 3a \rightarrow 4a$ takes *ca.* 40 h. In the case of 4a, the structure of the intermediate 3a was also confirmed by NMR spectroscopy of a mixture recorded 1 h after the start of the reaction. 4H-Thiopyran 4a was also obtained by treating 4Hpyran 3a directly with P_4S_{10} . The effect of substituents Ar, Ar¹ or Ar^2 on the rate of formation of 4b-m and 7, for which analogous 4H-pyran intermediates 3b-m and 6 have been identified chromatographically, can be seen from the data in Table 1.

Using these data, we suggest the following mechanism for formation of 4H-thiopyrans 4 and 7. The first stage obviously involves a dehydration process. The second stage involves an

Table 1 Analytical and IR data for the 4H-pyrans 3, 6 and the thiopyrans 4, 7

Comment	Desetien	V:-14			Found	Found (%) (Required)			Ξ(D in a)/	
(Formula)	time/h	(%)	Solvent	M.p./°C	с	Н	S	Halogen	$v(\text{Ring})/cm^{-1}$	
3c	4	55	heptane	215-216	88.9	7.7			1675, 1650	
$(C_{37}H_{38}O)$ 3j	4	60	heptane	137–138	(89.1 89.0	7.7 7.8	_	—) —	1690, 1640	
(C ₃₇ H ₃₈ O) 3I	4	48	heptane	123–124	(89.1 82.45	7.7 5 4.5	_	—) 9.3	1689, 1646	
(C ₂₉ H ₂₀ F ₂ O) 3m	4	44	heptane	100-103	(82.4 64.0	4.7 3.7		9.0) 29.1	1680, 1640	
$(C_{29}H_{20}Br_{2}O)$ 4a	40	72	heptane	160–161 <i>ª</i>	(64.0 86.5	3.7 5.6	 8.0	29.4)	1599, 1574	
(C ₂₉ H ₂₂ S) 4b	10	45	EtOH	197–199	(86.5 80.4	5.5 5.7	8.0 7.0) 	1604, 1573	
$(C_{31}H_{26}O_2S)$ 4c	8	60	EtOH	123-126	(80.5 86.5	5.7 7.6	6.9 6.4	—) —	1595 1573	
$(C_{37}H_{38}S)$	15	70	hentane	177_178	(86.3	7.4	6.2 7 35	—) —	1596 1576	
$(C_{31}H_{26}S)$	50	56	heptane	157 150	(86.5	6.1	7.4	—))	1596, 1570	
$(C_{29}H_{20}F_2S)$	50	J0 45	Etou	155 157	(79.4	4.9	7.3	8.7)	1595, 1570	
$(C_{29}H_{20}Br_2S)$	38	45	EIOH	155-157	62.4 (62.2	3.7	5.9 5.7	28.7 28.5)	1596, 1580	
4g (C ₃₀ H ₂₄ S)	38	74	heptane	158-161*	86.6 (86.5	5.7 5.8	7.7 7.7	— —)	1600, 1586	
$\begin{array}{l} \mathbf{4h} \\ (C_{29}H_{21}ClS) \end{array}$	46	61	heptane	169170	79.4 (79.7	5.0 4.8	7.5 7.3	8.1 8.1)	1598, 1576	
4i (C ₂₉ H ₂₁ BrS)	37	68	heptane	160–162 <i>ª</i>	72.5 (72.35	4.4 4.4	6.9 6.65	16.4 16.6)	1595, 1580	
4j (C ₃₇ H ₃₈ S)	44	54	EtOH–C ₆ H ₆	207–208	86.3 (86.3	7.4 7.4	6.1 6.2	— —)	1598, 1574	
4k (C ₃₁ H ₂₆ S)	40	66	Me ₂ CO–EtOH	101-103	86.5 (86.5	6.3 6.1	7.5 7.4)	1600, 1575	
41 $(C_{29}H_{20}F_{7}S)$	42	87	EtOH	157–159	79.4 (79.4	4.4 4.6	7.2 7.3	b 8.7)	1602, 1576	
$\frac{4m}{(C_{20}H_{20}Br_{2}S)}$	46	65	EtOH-C ₆ H ₆	168–170	62.2	3.8 3.6	5.4 5.7	28.6 28.5)	1600, 1574	
6 (CaoHaoO)	4	55	heptane	171–173	90.2	5.3)	1680, 1644, 1600	
$\frac{(2)^{2}}{7}$	45	70	EtOH-C ₆ H ₆	185–186	86.8	5.4	8.0 7 95)	1600, 1572	
 					(01.0	5.0	1.95	— <u> </u>		

^a Ref. 9 gives m.p. 157-157.5 °C. ^b Irreproducible results, m/z 438 (M⁺). ^c Ref. 10 gives m.p. 158-160 °C. ^d Ref. 4 gives m.p. 161-162 °C.



Fig. 1 HPLC analysis of the transformation of 1,3,3,5-tetraphenylpentane-1,5-dione 2a into 2,4,4,6-tetraphenyl-4*H*-thiopyran 4a via 4*H*pyran intermediate 3a

$$2 + P_4S_{10} \longrightarrow 3 + P_4OS_9 + H_2S_9$$

interaction between the electrophilic C-centres of the 4H-pyran intermediate 3 and nucleophilic S-centres of the agent, resulting in the formation of 4H-thiopyran 4 via a transition state probably with the structure shown in Scheme 1.



Interpretation of NMR Spectra.—For all newly prepared heterocyclic compounds their ¹H and ¹³C NMR spectra were recorded and interpreted (Tables 2 and 3); the complete assignments of the individual signals were based on the similarity of structures of the investigated compounds 4a-m and 7 to analogous 4H-pyrans 3 and 1,4-dihydropyridines 1, X = NR studied previously.^{2,6,19} Compounds 1, X = SO and SO₂, 4a, 6 and 7, which contain only unsubstituted phenyl groups, were used as models. They were subjected to a series of homonuclear and heteronuclear (¹H-¹³C) 2D NMR experiments, the interpretation of which allows the assignment of severely overlapped proton signals. Spectra of the remaining compounds 4b-m were attributed by analogy, with the spectra of the model compounds. It should be pointed out that the previous assignment ¹⁹ of the ¹³C NMR spectrum of 4*H*-thiopyran **4a** needs a correction: the signals for C-2 and C-2 (*ipso*) should be interchanged.

The interpretation of the ¹H NMR spectra has always been started by the assignment of the least shielded 2-H(*ortho*) resonance followed by the assignment of the corresponding 2-H(*meta*) signal by means of COSY.²⁰ Since chemical shifts of the protons in *meta* and *para* positions differed very little from each other, and their signals were situated in a crowded aromatic region, it was necessary to utilize the HOHAHA* experiment.²¹ This made it possible to correlate directly 2-H(*ortho*) and 2-H(*para*) resonances by magnetization transfer through 2-H(*meta*). In those cases, where both resonances were degenerate, causing the correlation peaks 2-H(*ortho*)-2-H(*meta*) and 2-H(*ortho*)-2-H(*para*) to overlap, valuable information was extracted from a two-quantum DQ-COSY experiment.²²

As for phenyl groups bound in position 4 of the heterocyclic skeleton, their protons are not so strongly deshielded as the analogous ortho-protons in the 2,6-phenyl groups and therefore 4-H(ortho) signals are overlapped by many other aromatic proton signals. Their entirely unambiguous assignment was made only for model compounds 1, X = SO and $SO_2, 4a, 6$ and 7 in parallel with the assignment of the ¹³C NMR resonances using the shapes of correlation peaks in heterocorrelated spectra.²³ The HEHAHA experiment, a heteronuclear version of the HOHAHA experiment,^{24,25} was also used. This pulse sequence allows the magnetization to be transferred during the spin-lock (sequence MLEV-17) over the ¹H coupling network and, by means of the imposed INEPT sequence, subsequently transferred to the ¹³C system. The practical consequence is a recording of the ¹H-¹³C correlation peaks not only of directly bound partners, but also of the so-called 'relay crosspeaks' linking hydrogen and carbon atoms separated by more than one σ -bond. By using the sequence just mentioned, we obtained information about the correlation of each individual ¹³C-centre with the whole ¹H-coupling network of the given benzenoid ring in a single experiment. It enabled us to assign proton signals of both 4,4-phenyl groups and, in combination with the one-bond heterocorrelated experiment, also the ¹³C-system with the exception of quaternary carbon atoms. They were later assigned employing the 'long-range INEPT' method optimized for the magnetization transfer through ${}^{3}J_{CH} = 7-8$ Hz.²⁶ In the case of heterocycles 6 and 7 the assignment of both proton and carbon signals was easier owing to a larger spread of ¹H resonances.

As has been mentioned, in the ¹H NMR spectra the 2-H-(*ortho*) signals are the most downfield shifted resonances, probably owing to a magnetic anisotropy effect of the pyranoid heterocyclic skeleton. This, however, does not hold for 4-H-(*ortho*) protons, the signals of which lie in the crowded aromatic region 7.10-7.30 ppm. Some additional effects of *para*substituents could be anticipated. Chemical shifts of C-2 and C-3 demonstrate the opposite polarity of the heterocyclic π electronic system, as is obvious for the compounds of types 1, X = SO, SO₂, and 4, respectively. In the case of sulfoxide 1, X = SO, the symmetry plane of the averaged conformation of the heterocyclic ring is disturbed, so that the two 4-phenyl groups are magnetically non-equivalent in both the ¹H and ¹³C NMR spectra (Tables 2 and 3).

Photocolouration Process.—Photocolouration characteristics of 4*H*-thiopyrans 4a-m and 7 are summarized in Table 4. 4-Substituents in the groups Ar, Ar¹ and Ar² have only a weak influence on the photochromic behaviour of the substances. This suggests that the coloured species are all of the same nature, in agreement with the proposed 4,8 alternative formulae 8 and 9, respectively. The position of the absorption maxima in



acetonitrile or chloroform solution, and the position of the photochromic maxima of the polycrystalline samples in MgO powder are presented in Table 4. The materials were illuminated for 180 s with a high pressure 200 W mercury discharge lamp. Column A represents the relative absorbance after sample illumination. The irradiated samples showed changes in two absorption regions. The longest wavelength bands seem to be the pure photochromic ones. The short wavelength shoulders are mostly connected with the formation of photodegradation products.

To acquire a deeper insight into the photodegradation process we have preparatively investigated the photoproducts from 4H-thiopyrans 4a, 4d and 4e in solution and in the solid state. In the first case we isolated the expected 4,15 2H-thiopyran 10a, but its structure differed from that proposed by Pirelahi and co-workers.³ However, 'unexpected' 2H-thiopyrans 10d and 10e were obtained in disagreement with the reaction pathway proposed by Mori and Maeda.⁴ In addition, the bridged non-photochromic intermediate 11a, previously observed⁴ only by NMR spectroscopy, was successfully isolated after a time-limited irradiation of 4a. Hence, the following plausible mechanism for the whole colouration-bleaching process may be expressed in the form below.



From Table 4 it can further be seen that the introduction of a *para*-substituent R (except R = Bu') into the 2,6-phenyl residues leads to bathochromic shifts of λ_{max} ; the magnitude of these shifts for different substituents are in the following order: F > OMe > Br > Me. In contrast, a weak effect was observed for *para*-substituents R^1 and R^2 of the 4,4-phenyl groups, as expected considering the formulae 8 and 9. It must, however, be pointed out that the photochromic band may be a superposition of the absorptions of 8 and 9 in the case of illuminated 4*H*-thiopyrans 4*g*-i and generally consists of several overlapping bands due to different conformational and vibronic structures of 8. These facts impeded an estimation of the accurate shift trends.

Kinetics of the Bleaching Process.—The thermal course of bleaching of solid 4H-thiopyran 4a at different temperatures is given in Fig. 2. The curves show normalized concentration [M(t)]/[M(0)] vs. t, of the coloured species 8a, calculated using the Munk-Kubelka function.²⁷

Basically, this shape could represent the superposition of

^{*} Homonuclear Hartmann-Hahn.

Table 2 ¹H NMR spectroscopic data for 4H-pyrans 3, 6 and 4H-thiopyrans 4, 7 (CDCl₃)

	δ (multiplicity and J/Hz)							
Compound ^a	H-2(<i>o</i>)	H-2(<i>m</i>)	H-2(<i>p</i>)	H-3	H-4(<i>o</i>)	H-4(<i>m</i>)	H-4(<i>p</i>)	CH ₃
1(X = SO)	7.68	7.42*	7.39 <i>^b</i>	6.67	7.39 ^{<i>b</i>}	7.38*	7.30 ^{<i>b</i>}	
· (50)	(m)	(m)	(m)	(s)	7.28 ^b	7.37 "	7.28 ^{<i>b</i>}	
	()	()		(-)	(m)	(m)	(m)	
$1(X = SO_{2})$	7.70	7.41 ^b	7.39 <i>°</i>	6.71	7.37 "	7.41 ^b	7.11 ^b	
. 27	(m)	(m)	(m)	(2)	(m)	(m)	(m)	
3c	7.70	7.41		5.72	7.28	-7.34	7.18	1.37
	(d, 8.7)	(d, 8.7)		(s)	(m)		(m)	(s)
3j	7.76		7.20-7.42°	5.76	7.20	–7.42°		1.30
•	(m)		(m)	(s)	(m)			(s)
31	7.75		7.44-7.32	5.68	7.27	7.02	-	
	(m)		(m)	(s)	$(dd, 8.8, 5.3^d)$	$(dd, 8.7, 8.7^d)$		
3m	7.74		7.34–7.41	5.64	7.44	7.17		
	(m)		(m)	(s)	(d, 8.5)	(d, 8.5)		
4a	7.60	7.36 <i>°</i>	7.35 <i>°</i>	6.24	7.33 <i>°</i>	7.33 %	7.23	
	(m)	(m)	(m)	(s)	(m)	(m)	(m)	
4b	7.53	6.89		6.25	7	.27–7.37	7.22	3.84
	(d, 8.9)	(d, 8.9)		(s)	(1	m)	(m)	(s)
4 c	7.54	7.38		6.23	7	.29–7.34	7.21	1.32
	(d, 8.6)	(d, 8.6)		(s)	(1	m)	(m)	(s)
4d	7.48	7.16	<u> </u>	6.21	7	.28-7.36	7.22	2.38
	(d, 8.2)	(d, 8.2)		(s)	()	m)	(m)	(s)
4 e	7.55	7.06	-	6.17	7	.27–7.39	7.24	
	$(dd, 8.7, 5.7^d)$	(dd, 8.6,	8.6^{d})	(s)	(1	m)	(m)	
4f	7.47	7.42	_	6.24		7.36–7.21		<u> </u>
	(d, 8.7)	(d, 8.7)		(s)		(m)		
4g	7.59		7.12–7.39°	6.25		7.12–7.39°		2.34
	(m)		(m)	(s)		(m)		(s)
4h	7.58		7.20–7.38°	6.18		7.20–7.38°		<u> </u>
	(m)		(m)	(s)		(m)		
4 i	7.58		7.21–7.46°	6.20		7.21–7.46°		
	(m)		(m)	(s)		(m)		
4j	7.59		7.28–7.38°	6.22	7.28–7.38°	7.23		1.30
	(m)		(m)	(s)	(m)	(d, 7.7)		(s)
4k	7.59		7.27–7.40	6.23	7.11	7.21		2.32
	(m)		(m)	(s)	(d, 8.1)	(d, 8.1)		(s)
41	7.58		7.32–7.40	6.16	7.25	7.03	_	_
	(m)		(m)	(s)	(dd, 8.9, 5.3")	(dd, 8.9, 8.9")		
4m	7.56		7.30–7.40	6.12	7.15	7.46		
	(m)		(m)	(s)	(d, 8.5)	(d, 8.5)		
6	7.72"	7.37"	7.31 °	5.10	7.51	7.31 ^{o.e}	7.37°	
_	(m)	(m)	(m)	(s)	(d, 7.4)	(m)	(m)	
7	7.55	7.31"	7.28 "	5.62	7.64	7.33 ** 3	7.40	—
	(m)	(m)	(m)	(s)	(d, 7.4)	(m)	(ddd, 7.4, 7.4, 1.1)	

^a Abbreviations: (*o*), ortho, (*m*), meta and (*p*), para. The number denotes the position of the phenyl group. ^b Overlapping signals. ^c Unresolved multiplet. ^d J_{H-F} . ^e See formula **6**, the signal of 4(*m*') lies at δ 7.73^b (m). ^f See formula **7**, the signal of 4(*m*') lies at 7.73 (d, 7.5).



Fig. 2 Decay curves for thermal bleaching of the normalized reactant concentration [M(t)]/[M(0)] of 2,4,4,6-tetraphenyl-4*H*-thiopyran 4a (polycrystalline sample mixed with MgO, 1:3) at various temperatures in air: (a), T = 288 K; (b), T = 304 K; (c), T = 313 K; (d), T = 333 K.

several exponentials, but the use of statistical distribution of thermodynamic reaction parameters seems to be a more sensible approach because of the linear log $\{[M(t)]/[M(0)]\}$ vs. t relation, as follows from Fig. 3. The optical properties of disordered polycrystalline materials 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 law for these dispersive processes²⁸ differs from the pure exponential form and follows $exp(-t^{\alpha})$, where t is the time and α is the dispersion parameter which measures the strength of dispersion. Hence the photochromic bleaching process could be described by a stretched exponential [eqn. (1)]^{29,30} where $0 < \alpha < 1$ measures the

$$[\mathbf{M}(t)] = [\mathbf{M}(0)]\exp[-(vt)^{\alpha}]$$
(1)

deviation from the pure exponential behaviour and v is the decay rate constant. In irregular systems, such as our poly-

Table 3 ¹³C NMR spectroscopic data for 4H-pyrans 3, 6 and 4H-thiopyrans 4, 7 (CDCl₃)

Compound ^a	C-2	C-2(<i>i</i>)	C-2(<i>o</i>)	C-2(<i>m</i>)	C-2(<i>p</i>)	C-3	C-4	$C-4(i)^{b}$ C-4(<i>i</i>) ^c	C-4(<i>o</i>) ^{<i>b</i>} C-4(<i>o</i>) ^{<i>c</i>}	$C-4(m)^{b}$ C-4(m) ^c	$C-4(p)^{b}$ C-4(p) ^c	CH ₃ CMe ₃
1(X = SO)	138.57	135.63	128.04	128.89	129.10	135.57	54.54	144.08	128.28	129.05	127.62	
1(X - SO)	138.80	130.90	120 30	128 71	178.60	120.26	57 17	143.03	127.97	128.99	127.60	
$1(x - 50_2)$	150.07	150.90	129.39	120.71	120.09	159.50	52.17	142.01	126.02	129.20	128.02	_
3c	147.04	131.64	124.57	125.26	149.73	103.44	47.37	151.68	127.97	128.33	126.05	31.28
3j	146.62	134.50	124.76	128.34	128.41	104.40	46.43	146.55	127.55	125.22	148.82	34.64 31.40
31	147.15	133.99	124.79	128.46	128.78	103.58	46.40	145.16	129.42	115.27	162.28	34.40
								$(2.9)^{d}$	$(7.8)^{d}$	$(21.4)^{d}$	$(245.7)^{d}$	_
3m	147.56	133.83	124.81	128.47	128.88	102.91	46.90	148.04	129.63	131.60	148.04	—
4a	131.27	138.47	126.63	128.58	128.58	123.18	53.41	148.36	128.20	128.44	126.31	_
4b	131.07	130.86	127.85	113.92	159.91	122.73	53.42	148.64	128.19	128.37	126.23	55.37
4c	131.07	135.67	126.27	125.48	151.69	123.31	53.40	148.54	128.23	126.37	126.23	31.29
4d	131.18	138.44	126.47	129.22	135.68	123.18	53.36	148.55	128.20	128.44	126.31	21.18
4 e	130.26	$(3.2)^d$	128.42	115.53 (21.6) ⁴	163.04	124.00	53.48	148.77	128.12	128.51	126.46	
4f	130.14	137.15	128.08	131.72	122.66	124.34	53.43	147.88	128.16	128.56	126.53	_
4g	131.06	138.54	126.62	128.56	128.50	124.00	53.06	148.52	128.18	128.41	126.28	
4 b	121 95	129 26	126.63	179 60	128 60	122.20	52.04	145.50	128.07	129.15	135.90	20.98
-411	151.65	136.20	120.05	120.09	120.09	125.50	55.04	146.02	128.08	128.38	120.34	
4 i	131.90	138.25	126.64	128.64	128.71	123.22	53.12	147.96	129.09	128.58	126 55	
								147.27	129.97	131.54	120.46	
4j	130.42	138.67	126.60	128.53	128.41	124.19	52.55	148.95	127.80	125.26	145.44	31.39
4k	130.85	138.63	126.64	128.55	128.46	124.19	52.73	145.66	128.07	129.13	135.85	20.98
41	131.81	138.19	126.64	128.67	128.77	123.37	53.38	144.00	129.66	115.33	161.40	
4m	132.51	138.05	126.64	128.69	128.86	122.60	52.84	(3.0) <i>*</i> 146.87	(8.0) <i>*</i> 129.85	(21.4) <i>*</i> 131.69	(246.0) <i>ª</i> 120.72	
6	139.15	134.24	124 57	128 38	128 50	101 03	49.86	149 45	126 50 °	127 90 °	128.02	
v	137.13	137.27	1	120.00	140.30	101.05	77.00	177.75	120.30	127.70	120.02	
7	132.43	138.51	126.45	128.56	128.48	120.05	55.57	153.57	126.40 ^f	128.12 ^f	128.19	

^{*a*} Abbreviations: see Table 2. ^{*b*} Phenyl group bearing the substituent R¹. ^{*c*} Phenyl group bearing the substituent R². ^{*d*} J_{C-F} . ^{*e*} See formula 6, the signals C-4(o') and C-4(m') lie at δ 139.10 and δ 119.77 respectively. ^{*f*} See formula 7, the signals C-4(o') and C-4(m') lie at δ 139.01 and δ 119.90 respectively.

 Table 4
 Solution and photochromic solid state absorption maxima

Starting 4 <i>H</i> -thiopyran	R	R ¹	R ²	λ_{\max}^{a}/nm	$\log \epsilon^{b}/\epsilon/\lambda \ dm^3 \ mol^{-1} \ cm^{-1}$	λ _{max} ^c /nm	A ^d
4a	н	Н	Н	250 ^b	4.47	(381), 564	0.6
4b	OMe	Н	Н	260	4.62	(394), 600	0.3
4c	Bu ^r	н	Н	242	4.57	(382), 545	0.4
4d	Me	Н	Н	242	4.57	(399), 572	0.3
4e	F	н	Н	250 ^b	4.34	(393), 602	0.4
4f	Br	Н	Н	255 ^b	4.62	(398), 594	0.3
4g	Н	Me	Н	255 ^b	4.62	(380), 547	0.3
4h	Н	Cl	Н	250 <i>°</i>	4.46	(388), 567	0.3
4i	Н	Br	Н	238	4.53	(387), 564	0.3
4j	Н	Bu ^t	Bu ^t	250 ^b	4.00	(378), 552	0.1
4k	Н	Me	Me	238	4.57	(359, 404), 598	0.2
41	Н	F	F	238	4.51	(384), 559	0.2
4m	Н	Br	Br	250 ^b	4.57	(362), 554	0.2
7		_		262 <i>^b</i>	4.67	(393, 442), 666	0.2

^a Solution in acetonitrile. ^b In chloroform. ^c Polycrystalline powder in MgO after 180 s illumination by a high pressure 200 W mercury discharge lamp; the data in parentheses denote shoulders. ^d Relative absorbance.

crystalline material, the activation energies and entropies of the photochromic back reaction depend on the local geometry around the reacting species $\mathbf{8}$, and consequently are quantities with statistical variation. The thermally-induced back reaction is associated with the rate constant v(E) according to eqn. (2) where v_0 is the frequency factor. Since the energy difference

$$v(E) = v_{o} \exp[-(E_{m} - E)/kT]$$
 (2)



Fig. 3 Semi-logarithmic plot of the normalized reactant concentration [M(t)]/[M(0)] vs. t^{α} (data from Fig. 2). Values of α were resolved by least-square fits to the corresponding decay curves (the scale t^{α} refers to different α values).



Fig. 4 Dependence of the logarithm of rate constant v on the reciprocal temperature



Fig. 5 Dispersion parameter α derived from the calculated [M(t)] curves [eqn. (1)] as a function of the fluctuation σ of the activation energy for thermal bleaching: T = 288 K, $\nu_0 = 37$ s⁻¹ and $E_m - E_0 = 0.33$ eV

between the ground state (E) and the maximum of the energy barrier (E_m) depends on a set of conformational parameters, each varying statistically, the most probable distribution



Fig. 6 Decay curves for thermal bleaching of 2,4,4,6-tetraphenyl-4*H*-thiopyran 4a (polycrystalline sample mixed with MgO) given as the Munk-Kubelka function K/S vs. time: (a), in air, T = 313 K; (b), in a vacuum (2 × 10⁻³ Pa), T = 313 K; (c), 10 h in vacuum (1 × 10⁻³ Pa), T = 333 K

function for $(E_m - E)$ was assumed by Richert and Bässler³⁰ to be a Gaussian one characterized by its width σ . Therefore, the time dependence of the concentration of coloured species 8 should be the convulation of first-order decay functions reflecting the unimolecular nature of the process and the distribution function for the reaction rates [eqn. (3)].²⁹ The

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

experimental results in air, given in Fig. 2, were fitted using eqn. (3). The best fits were obtained with the following parameters: T = 288, 304, 313 and 333 K; $\sigma = 0.033$, 0.030, 0.022 and 0.018 eV; $\nu = 8.42 \times 10^{-5}$, 1.30×10^{-4} , 1.73×10^{-4} and 3.63×10^{-4} s⁻¹.

The Gaussian widths of the distributions of the activation energies decrease with temperature. From the temperature dependence of the fitted parameter v the activation energy (Fig. 4) obtained was $(E_m - E_0) = (0.33 \pm 0.02)$ eV and the average frequency factor $v_0 = (37 \pm 2) \text{ s}^{-1}$. Thus, with respect to the temperature range 288 K < T < 340 K, the experimental data can be interpreted in terms of a single temperature-activated rate process, the only temperaturedependent quantity being the fluctuation of the activation energies. Fig. 5 shows a plot of the dispersion parameter α (obtained from the experimental [M(t)]/[M(0)] vs. t^{α} curves) as a function of the fluctuation σ of the activation energy derived from the calculated [M(t)] curves according to eqn. (3). The parameters used were T = 288 K, $v_0 = 37$ s⁻¹, $E_m -$ $E_0 = 0.33$ eV. One can see that the non-exponential dependence of the thermal bleaching reaction $8a \longrightarrow 4a$ can be accounted for by a gaussian distribution of activation energies whose width decreases with increasing temperature.

In a vacuum the bleaching process was much slower. The decay half-life was longer by ca. 1–2 orders of magnitude. Fig. 6 shows the decay curves at different ambient conditions. It is evident that the influence of dioxygen on the decay rate is greater than the influence of temperature. Also, for larger single crystals the bleaching was slower. Thus, the parameters of the bleaching process presented in this paper are characteristic of microcrystals of **4a** only.



Fig. 7 (a) Absorption spectra of solid 2,4,4,6-tetraphenyl-4H-thiopyran 4a (polycrystalline sample mixed with MgO, 1:3) at 293 K during repeated illumination by 200 W mercury discharge tube in air (see text for details): A, spectrum before UV exposure; B, C and D, spectra after the first, the second and the third colouration process, respectively. (b) Absorption spectra of 4a: A, before UV exposure; B, after UV illumination; E, after the thermal bleaching reaction

An interesting effect is also evident from Fig. 6. After the ending of the activating illumination in air the absorbance of the solid samples increased slightly even in the dark. This 'yo-yo effect' can be explained taking into account the partial reversibility of the reaction 8a = 11a. Compound 11a is in fact colourless (see Experimental section) and its molecular shape differs from those of 4a and 8a.

The background of the dispersive behaviour is generally unknown. Very often dispersive kinetics are applied to physical or chemical transformations occurring in irregular systems, even if the elementary step is a unimolecular reaction. In our case dispersive kinetics were found to be applicable to a photochromic reaction occurring in a polycrystalline material. Because of the short penetration length of UV colouring light and the highly specific surface, most of the excitations take place at the surface or in a layer close to the surface of microcrystals where the molecules are not embedded in a perfectly ordered matrix. Moreover, it has to be assumed that each of the excited species interacts in a somewhat different way or to a somewhat different extent with neighbouring molecules. The other fact, which can give rise to the dispersive kinetics, is the influence of dioxygen molecules. The reason seems to be the formation of a complex between electron-withdrawing oxygen and electronreleasing coloured species. Consequently, the rate of the back \rightarrow 4a should depend strongly on the crystal size reaction 8a of 4a, because the concentration of dioxygen in the bulk crystal is much lower than on its surface. Therefore, the crystal itself represents a locality with a set of individual processes of different rates, which are higher at the surface where the concentration of dioxygen molecules is higher. Hence, with larger crystals slower decolouration kinetics are observed.

Stability of the Colouration-Bleaching Process.—Figs. 7(a) and 7(b) show the absorption spectra taken after repeating colouration. Curves A represent the absorption before UV illumination of the sample **4a** in air. Curves B represent the absorption after UV exposure. After that the sample was kept in the dark for 24 h and illuminated once more [curve C in Fig. 7(a)]. The same procedure was applied to obtain curve D. From this picture it is evident that the colouration by UV light and thermal bleaching is reversible but a photodegradation does occur, as is clear from the decrease in the concentration of the coloured species after repeated illumination and the increase of the absorption at 380 nm. The latter effect is clearly visible from Fig. 7(b), curve E, which represents the spectrum after the bleaching reaction.

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Experimental

M.p.s were uncorrected and measured on a Boetius block. NMR spectra were recorded on a Bruker AM 400 spectrometer in CDCl₃ using Me₄Si as the internal standard. Coupling constants are in Hz. Experimental parameters: ¹H NMR (400.13 MHz), digital resolution 0.184 Hz/point, pulse width 4 μ s, temperature 297 K; ¹³C NMR (100.61 Hz), digital resolution 0.898 Hz/point, temperature 297 K. IR absorption spectra were recorded on a Perkin-Elmer 325 spectrophotometer in CHCl₃. HPLC analyses were carried out on a Separon SGX C18 column (3 \times 150 mm, 0.4 cm³ min⁻¹), particle size 5 μ m (Tessek, Czechoslovakia) in the system 10% H₂O in MeOH (v/v). Mass spectra were measured with a JEOL 303/DA 5000 apparatus (70 eV, direct input).

Substituted 2,4,4,6-tetraaryl-4*H*-pyrans **3a**-m were obtained^{1,19} from the 1,5-diketones **2a**-m and **5** with P_4O_{10} . Physico-chemical and spectral data of newly prepared 4*H*pyrans **3c**, **3j**, **3l**, **3m** and **6** are summarized in Tables 1-3. 2,4,4,6-Tetraphenyl-4*H*-thiopyran 1,1-dioxide (1, X = SO₂) was prepared by the oxidation⁹ of **4a** with hydrogen peroxide in acetic acid at elevated temperatures.

2,4,4,6-*Tetraphenyl*-4H-*thiopyran* 1-oxide (1, X = SO).—4H-Thiopyran **4a** (0.5 g) was dissolved in a mixture of acetic acid (20 cm³) and chloroform (20 cm³), and 30% hydrogen peroxide (1.4 cm³) was added. The mixture was stirred at 20 °C for 24 h, diluted with water (150 cm³) and extracted with chloroform. The organic layer was washed with saturated aqueous NaHCO₃ and water to neutral reaction, then dried (MgSO₄) and evaporated. The crude product was chromatographed on a column of silica gel (25 g) with benzene–acetone as eluent. Recrystallization from heptane–benzene gave 0.41 g (79%) of 1, X = SO, m.p. 172–173 °C; $\tilde{\nu}_{max}/cm^{-1}$ 1028 (SO); NMR characteristics, see Tables 2 and 3 (Found: C, 83.3; H, 5.5; S, 7.6. C₂₉H₂₂OS requires C, 83.2; H, 5.3; S, 7.7%).

General Procedure for the Preparation of 4H-Thiopyrans 4am and 7.—P₄S₁₀ (7.5 mmol) was added under dry nitrogen to a stirred solution of the corresponding 1,5-diketone (2.5 mmol) $2^{1.5,17,18}$ or 5^7 in xylene (40 cm³) at a bath temperature of 135– 140 °C. The composition of the reaction mixture was monitored by HPLC. After the intermediate 4*H*-pyran 3 had disappeared the mixture was cooled and filtered and the filtrate was evaporated at reduced pressure. The residue was dissolved in benzene and chromatographed on a column of silica gel (40 g). The oily products were usually stimulated to crystallization by the addition of a small amount of ethanol. The 4*H*-thiopyrans **4a**-m and 7 thus obtained were recrystallized from a suitable solvent as given in Table 1.

2,4,4,6-*Tetraphenyl*-4*H*-thiopyran 4a.—A reaction of 2,4,4,6tetraphenyl-4*H*-pyran 3a¹ (0.5 g) with P_4S_{10} (1.7 g) carried out as described above (reaction time 36 h) gave 0.32 g (60%) of 4a. In another experiment a solution of 1,3,3,5-tetraphenylpentane-1,5-dione 2a¹ in glacial acetic acid (30 cm³) was added to a solution of HCl (4 g) in the same solvent (30 cm³). The resulting mixture was then saturated with a gaseous HCl–H₂S mixture (6 h). The solvent was evaporated at reduced pressure and the residue was chromatographed on a column of silica gel (20 g) with benzene as eluent. Double crystallization from heptane gave 0.22 g (45%) of 4a.

General Procedure for Photolysis in Acetonitrile.—The reactions of 4H-thiopyrans 4a, 4d and 4e were performed in solutions (450 cm³) irradiated by a 400 W high-pressure mercury lamp from inside the solution without a filter at 20 °C in a thermostatically controlled bath under argon. All the photochemical reactions were monitored by HPLC and when the products 10 appeared in a suitable concentration irradiation was stopped. The solvent was evaporated at reduced pressure and the crude products 10 were recrystallized from ethanol.

2,3,4,6-*Tetraphenyl*-2H-*thiopyran* **10a**. According to the general procedure 4H-thiopyran **4a** (0.45 g) afforded its 2Hisomer **10a** as yellow crystals (68%), m.p. 155–156 °C; λ_{max} (MeCN) 368 nm (ε 9200 dm³ mol⁻¹ cm⁻¹); δ_{H} (CDCl₃) 4.89 (1 H, s, 2-H), 6.83 (1 H, s, 5-H) and 7.18–7.33 (16 H, m, aromatic H), 7.56 (2 H, m, 6-Ph, *ortho*), 7.59 (2 H, m, 2-Ph, *ortho*); δ_{C} (CDCl₃) 47.76 (C-2), 123.10 (C-5), 125.02 (C-6), 126.76, 127.01 (aromatic C, *para*), 127.59, 127.62, 127.85, 128.18, 128.39 (aromatic C, *ortho, meta*), 128.51, 128.68 (aromatic C, *para*), 129.48, 130.01 (aromatic C, *ortho, meta*), 132.71 (C-4), 137.08 (aromatic C, 2-Ph, *ipso*), 137.77 (aromatic C, 6-Ph, *ipso*), 141.02 (C-3), 141.31 (aromatic C, 3-Ph, *ipso*) and 141.65 (aromatic C, 4-Ph, *ipso*); *m/z* 402 (M⁺, 65%) (Found: C, 86.3; H, 5.9; S, 7.9. C_{2.9}H_{2.2}S requires C, 86.5; H, 5.5; S, 8.0%).

3,6-Bis(p-tolyl)-2,4-diphenyl-2H-thiopyran 10d. According to the general procedure 4H-thiopyran 4e (0.40 g) afforded its 2Hisomer 10d as yellow crystals (58%), m.p. 79-81 °C; λ_{max} . (MeCN) 366 nm (ϵ 10 300 dm³ mol⁻¹ cm⁻¹); $\delta_{\rm H}$ (CDCl₃) 2.22 (3 H, s, 3-Ar, Me), 2.32 (3 H, s, 6-Ar, Me), 4.87 (1 H, s, 2-H), 6.77 (1 H, s, 5-H), 6.87 (2 H, m, 3-Ar, meta), 6.94 (2 H, m, 3-Ar, ortho), 7.11 (2 H, m, 6-Ar, meta), 7.21-7.33 (8 H, m, aromatic H), 7.46 (2 H, m, 6-Ar, ortho), 7.59 (2 H, m, 2-Ph, ortho); $\delta_{\rm C}$ (CDCl₃, multiplicity caused by ¹H) 21.12, 21.16 (Me, q), 47.80 (C-2, d) 122.52 (C-5, d), 124.69 (C-6, s), 126.88 (aromatic C, d, 4-Ph, para), 127.41 (aromatic C, d, 2-Ph, para), 127.50 (aromatic C, d, 2-Ar, ortho), 127.64 (aromatic C, d, 6-Ph, ortho), 128.18 (aromatic C, d, 4-Ph, ortho), 128.33 (aromatic C, d, 2-Ph, meta), 128.56 (aromatic C, d, 3-Ar, meta), 129.10 (aromatic C, d, 6-Ar, meta), 129.34 (aromatic, d, 3-Ar, ortho), 130.27 (aromatic C, d, 4-Ph, meta), 132.24 (C-4, s), 134.98 (aromatic C, s, 6-Ar, ipso), 136.41 (aromatic C, s, 3-Ar, para), 136.62 (aromatic C, s, 2-Ph, ipso), 138.08 (aromatic C, s, 3-Ar, ipso), 138.67 (aromatic C, 6-Ar, para), 141.46 (C-3, s), 141.97 (aromatic C, s, 4-Ph, ipso); m/z 430 (M⁺, 60%) (Found: C, 86.5; H, 6.1; S, 7.5. C₃₁H₂₆S requires C, 86.5; H, 6.1; S, 7.3%).

3,6-Bis(4-fluorophenyl)-2,4-diphenyl-2H-thiopyran 10e. According to the general procedure 4H-thiopyran 4e (0.40 g) afforded its 2H-isomer 10e as yellow crystals (60%), m.p. 150-151 °C; λ_{max} (MeCN) 368 nm (ε 10 500 dm³ mol⁻¹ cm⁻¹); $\delta_{\rm H}({\rm CDCl}_3)$ 4.85 (1 H, s, 2-H), 6.74 (1 H, s, 5-H), 6.75 (2 H, m, 3-Ar, meta, J_{HF} 8.9 Hz), 6.98 (2 H, m, 6-Ar, meta, J_{HF} 8.2 Hz), 6.99 (2 H, m, 3-Ar, ortho, J_{HF} 5.4 Hz), 7.21-7.28 (5 H, m, 4-Ph), 7.26 (1 H, m, 2-Ph, para), 7.33 (2 H, m, 2-Ph, meta), 7.51 (2 H, m, 6-Ar, ortho, $J_{\rm HF}$ 5.4 Hz) and 7.56 (2 H, m, 2-Ph, ortho); $\delta_{\rm C}({\rm CDCl}_3,$ multiplicity caused by ¹H only) 47.78 (C-2, d), 114.87 (aromatic C, d, 3-Ph, meta, J_{CF} 21.4 Hz), 115.36 (aromatic C, d, 6-Ar, meta, J_{CF} 21.7 Hz), 122.84 (C-5, d), 123.78 (C-6, s), 127.19 (aromatic C, d, 4-Ph, para), 127.52 (aromatic C, d, 2-Ph, ortho), 127.70 (aromatic C, d, 2-Ph, para), 128.33 (aromatic C, d, 4-Ph, ortho), 128.52 (aromatic C, d, 2-Ph, meta), 129.39 (aromatic C, d, 6-Ar, ortho, J_{CF} 8.2 Hz), 129.93 (aromatic C, d, 4-Ph, meta), 131.10 (aromatic C, d, 3-Ar, ortho, J_{CF} 7.9 Hz), 131.71 (C-4, s), 133.79 (aromatic C, s, 6-Ar, ipso, J_{CF} 3.1 Hz), 136.89 (aromatic C, s, 3-Ar, ipso, J_{CF} 3.5 Hz), 137.17 (aromatic C, s, 2-Ph, ipso), 140.96 (C-3, s), 141.34 (aromatic C, s, 4-Ph, ipso), 161.50 (aromatic C, s, 3-Ar, para, J_{CF} 247.2 Hz) and 163.15 (aromatic C, s, 6-Ar, para, J_{CF} 249.1 Hz); m/z 438 (M⁺, 78%) (Found: C, 79.9; H, 4.6; S, 7.4. C29H20SF2 requires C, 79.4; H, 4.6; S, 7.4%).

Isolation of 1,3,5,6-Tetraphenyl-2-thiabicyclo[3.1.0]hex-3-ene 11a.—A solution of 4H-thiopyran 4a (250 mg) in ethanol (250 cm³) was irradiated for 5 min. Preparative HPLC (C18 bonded stationary phase, eluent gradient from water-methanol 1:4) gave, in addition to 180 mg of the mixture of 4a, 10a and 11a, a chromatographically pure sample of 11a as a yellow powder (11 mg, decomposed above 70 °C in the solid state and at 100 °C in toluene solution into 2*H*-thiopyran **10a**); λ_{max} (MeCN) 322 nm (ϵ 3200 dm³ mol⁻¹ cm⁻¹); δ_{H} (CDCl₃) 3.69 (1 H, s, 6-H), 6.10 (1 H, s, 4-H) and 7.00–7.52 (20 H, m, aromatic H); δ_{C} (CDCl₃) 27.36 (C-6), 54.13 (C-5), 56.26 (C-1), 120.48 (C-4), 126.14, 126.53, 127.01, 127.50, 127.58, 128.00, 128.14, 128.21, 128.44, 128.57, 130.42, 131.06 (aromatic C, *ortho, meta, para*), 133.65, 135.01, 138.16, 138.41, 142.89 (C-3 and aromatic C, *ipso*).

Solid State Photolysis of 2,4,4,6-Tetraphenyl-4H-thiopyran 4a.—Crystalline film, obtained by evaporation of a benzene solution of 4a (100 mg) inside an immersion photochemical reactor, was dried under an argon stream for 1 h and then irradiated by a 400 W high-pressure mercury lamp at 20 °C for 2 h. The ¹H NMR spectrum of the irradiated material showed that the starting 4*H*-pyran 4a contained 4% of the 2*H*-isomer 10a.

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