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PHOTOCHROMIC SPIROPYRANS

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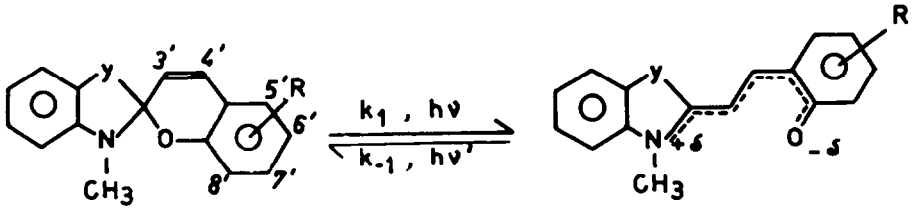
Abstract—The synthesis of new photochromic benzothiazolinospiropyrans has been described. The decolouration kinetics of the corresponding open-ring merocyanines have been followed using the spectrophotometric method. A strong negative solvatochromism corresponds to the influence of the polarity of the solvent.

The nature and the position of the substituents in the benzopyran and benzothiazoline moieties exerts a strong influence on the λ_{max} of absorptions and on the first-order decolouration rate constants. Activation energies and entropies were evaluated, and their differences discussed. Similarly the substituent on the heterocyclic benzothiazoline-nitrogen has been varied, and its influence examined.

Most of the data can be interpreted on the basis of the electron attracting and electron withdrawing properties of the substituents; some steric effects interfere in a few cases.

I. INTRODUCTION

THE photochromism of indolinospiropyrans[1,2] can be represented, in first approximation, by the following reaction scheme:



where Y represents $C(CH_3)_2$, k_1 and k_{-1} are the constants for the thermal reactions and $h\nu$ and $h\nu'$ are the UV and visible light energies required for the colouration and decolouration reactions respectively.[3–18]

The structure of the "open form" was assigned on the basis of the similarity of its solvatochromic behaviour with that of merocyanines, and supported by chemical evidence.[19] Several spiropyran photochromes containing different heterocyclic nuclei connected with the benzopyran moiety have been described in the literature.[2,19,20–23] Substitution of the indoline nucleus in the above spiropyran by the benzothiazoline ring (Y=S) gives a non-photochromic system on account of the high stability of the merocyanine derivative.[25] However, introduction of a Me group at C-3' reduces the stability of the merocyanine to such an extent that the system recovers its photochromic properties.[21–26]

The aim of the present work was the study of the influence of the solvent polarity and of the steric and electronic properties of substituents on the kinetics of the decolouration reaction of benzothiazoline spirobenzopyrans.

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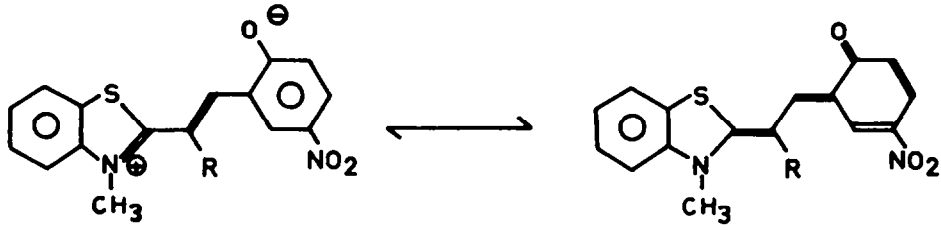
II. EXPERIMENTAL RESULTS

The visible absorption spectrum of N-methyl-6'-nitrobenzothiazoline spirobenzopyran and its 3'-methyl homologue have been measured after UV irradiation. The results are given in Table 1 in decreasing order of the polarity of the solvents

TABLE 1. INFLUENCE OF SOLVENT POLARITY ON THE λ_{max} OR MEROCYANINES (in *nm*) (T = 20°)



Solvent	E_t[28]	R = H	R = CH_3
Methanol	55·5	506	sh
Ethanol	51·9	514	sh
Isopropanol	48·6	527	469
Acetonitrile	46·0	542	496
Dimethylformamide	43·8	552	504
Acetone	42·2	556	523
Methylene chloride	41·1	568	543
Pyridine	40·2	569	546
Chloroform	39·1	573	549
Dimethoxyethane	38·2	570	
Chlorobenzene	37·5	593	574*
Tetrahydrofuran	37·4	575	558*
Dioxane	36·0	584	
Toluene	33·7	601	

sh = shoulder band
* = at 2°C

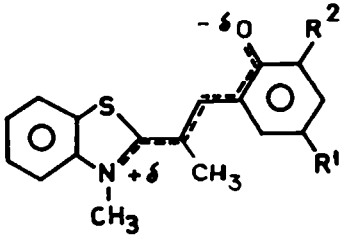
as measured by Dimroth's scale.[28] Table 1 shows that the visible absorption spectra of the merocyanine and of the "open form" of the spiropyran both exhibit a strong bathochromic shift as the polarity of the solvent decreases; as in the case of the indolinospiropyrans,[2] a first order kinetic relationship is observed for the decolouration reaction of benzothiazolinospiropyrans.

The kinetic data for two spiropyrans are given in Table 2. It was found that the values of the rate constants were independent of the initial spiropyran concentration in the range 10^{-3} to 5×10^{-5} M, and independent of the initial merocyanine concentration (optical densities 0·2 to 2). Moreover these spiropyrans are not thermochromic so that the decolouration reaction is not complicated by a thermal colouration reaction.

The data in Table 2 demonstrate that the rate of the decolouration reaction is considerably reduced as the solvent polarity is increased. The 6'-nitroderivative

TABLE 2. INFLUENCE OF THE POLARITY OF THE SOLVENT ON THE DECOLOURATION REACTION

$(spiran)_0 = 1 \pm 0{\cdot}1 \times 10^{-3}$ mole l^{-1}. $\lambda_{irrad} \geqslant 304$ nm; cell thickness: 1 cm.



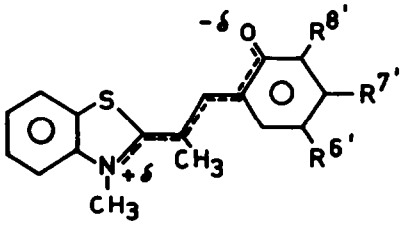
Solvent	E_t(Kcal/mole)	$R^1 = NO_2$ $R^2 = H$				$R^1 = Br$		$R^2 = NO_2$	
		t°C	$k_{1\,min^{-1}} \times 10^{-3}$	E_a kcal/mole	log A	t°C	$k_{1\,min^{-1}} \times 10^{-3}$	E_a Kcal/mole	log A
Acetonitrile	46·0	15·9	5·2			31·9	1·4		
		21·9	12·1			39·9	4·5		
		27·7	34·6	28·2 ± 0·5	19·1	48·0	15·9	29·6 ± 0·3	18·4
		32·2	64·7			55·1	42·7		
		36·7	132·6						
Butanone	42·2	2·4	15			28·1	8·0		
		9·2	45·1			32·3	17·7		
		14·3	95	22·7 ± 0·5	16·3	36·7	31·7	28·8 ± 0·8	18·8
		20·0	196 ± 5			40·7	58·1		
		32·3	924			45·6	96·5		
Pyridine	40·2	2·4	6·2			26·4	20·5		
		5·0	10·5			31·2	37·2		
		9·2	23·6	27·55 ± 1·2	19·7	35·5	65	23·1 ± 0·4	15·2
		14·5	80·3			39·4	95		
		20·2	110						
Tetrahydrofuran	37·4	2·2	130			16·4	23·2		
		5·0	190	19·6 ± 0·6	14·7	26·5	81·8	21·8 ± 0·2	14·9
		9·2	320			30·5	133		
		14·5	600			32·2	161		

[a]: E_t value for acetone

($R^1 = NO_2$) has an anomalously low decolouration rate in pyridine solution, taking into account the polarity of this solvent; whereas the 6-bromo 8′-nitro derivative shows the expected correlation between rate of decolouration and solvent polarity. This anomalous behaviour was observed for *all* the 6′-nitrospyrans which were synthesized, while never for the 8′-nitrospirans.

TABLE 3. INFLUENCE OF SUBSTITUENTS IN THE BENZOPYRAN MOIETY ON THE DECOLOURATION RATE

$(spiran)_0 = 5 \pm 0{\cdot}5 \times 10^{-3}$ mole l^{-1}; cell thickness = 1 cm
$\lambda_{irrad} = 366$ nm; $T = 20°C$; solvent: dimethylformamide



Substituents				$k \times 10^{-3}$ (min^{-1})	λ_{max}[d] (visible spectrum)
$R^{5'}$	$R^{6'}$	$R^{7'}$	$R^{8'}$		
Benzo		H	H	[a]	—
H	I	H	I	[a]	
H	Br	H	Br	[a]	—
H	CH_3	H	NO_2	very large	—
CH_3	NO_2	H	i-C_3H_7	1180 ± 160[b]	420 sh[e]
H	Br	Cl	Br	510 ± 5[c]	—
H	H	H	NO_2	450 ± 13	536
H	NO_2	H	t-C_4H_9	142 ± 3	519
H	NO_2	H	CH_3	135 ± 1	517
H	NO_2	H	H	24 ± 0·8	496
H	SO_2F	H	H	8·3 ± 0·1[c]	477[c]
H	Br	H	NO_2	0·83 ± 0·05	473

[a] no photochromism;
[b] approximate value;
[c] irradiation must be carried out in the presence of benzophenone, otherwise no photochromism is observed;
[d] measured in acetonitrile;
[e] shoulderband.

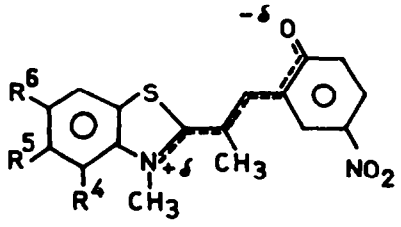
The values of the activation energies and activation entropies are also strongly dependent on the solvent polarity, i.e. E_a and log A_{exp} increase strongly with increasing solvent polarity. Again, the 6′-nitro compound behave anomalously in pyridine, the activation energy and entropy being much larger in this solvent than in butanone although the polarity E_t-values are in reverse order.

The influence of substituents on the kinetics of the decolouration reaction has been examined as a function of their position in the molecule. For substituents in the benzopyran moiety, the decolouration constants are given in Table 3.

This table shows that the decolouration rate constant diminishes strongly as the electronegativity of the substituents increases. Moreover, photochromism can only be observed when the electron withdrawing character of the substituents is sufficiently high; it also depends, of course, on the temperature and on the nature of the solvent. Since decolouration rates of the 6′-nitro 8′-methyl and 6′-nitro 8′-t-butyl derivatives are identical there is no steric effect at the 8′ position. In contrast, introduction of a Me group at the 5′ position has a marked effect on the decolouration rate constant of the spiropyran, as well as on the visible absorption maximum (more than 100 nm

TABLE 4. INFLUENCE OF THE SUBSTITUTION IN THE BENZOTHIAZOLINE RING ON THE DECOLOURATION KINETICS

$(spiran)_0 = 2{\cdot}5 \pm 0{\cdot}2 \times 10^{-3}$ mole l^{-1}; cell thickness = 1 cm
solvent: dimethylformamide; $\lambda_{irrad} \geqslant 304$ nm



	temp °C	k × 10^{-2} min^{-1}	E_a Kcal/mole	log A
6-Chlorobenzothiazoline	10	3·3		
	15	5·8		
	20	12·9	22·7 ± 0·5	16·1
	27	30·7		
Benzothiazoline	20	2·4		
	27	5·7		
	30·7	8·4	21·6 ± 0·5	14·5
	36	15·9		
4-Methylbenzothiazoline	20	1·8		
	27	4·2		
	31	6·8	22·0 ± 0·4	14·7
	36	12·6		
6-Methylbenzothiazoline	20	1·1		
	27	2·8		
	30·7	3·4		
	36	6·4	20·8 ± 0·9	13·6
	40	11·8		
6-Methoxybenzothiazoline	20	0·6		
	27	1·3		
	30·7	1·7	17·6 ± 0·8	10·9
	36	2·6		
	40	4·5		
5-Isobutyramidobenzothiazoline	30·7	6·2		
	35	9·2		
	40	17·0	22·2 ± 1·1	14·8
	45	26·9		
	50	57·2		

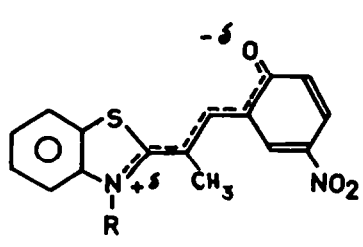
difference). The last column of Table 3 shows a regular bathochromic shift of the λ_{max} of the merocyanine as the electronegative character of the substituents increases.

The influence of the nature and position of the substituents in the benzothiazoline moiety on the kinetics of the decolouration reaction has also been examined. As shown in Table 4, this influence is much less pronounced than in the preceeding cases where the substituents were present in the benzopyran moiety. An increase in the electronegativity of the substituents causes an acceleration of the decolouration reaction. The activation energies and entropies vary only slightly with the nature of the substituents, excepted in the case of the 6'-methoxy derivative, where both values are particularly low.

The influence of substitution at the heterocyclic nitrogen on the decolouration kinetics is of particular interest since it might give an indication of the nature of steric and electronic effects at the center of the photochrome itself.

TABLE 5. INFLUENCE OF SUBSTITUENTS ON THE HETERO-N-ATOM ON THE DECOLOURATION KINETICS

(spiran)$_0$ = 1 ± 0·1 × 10^{-3} mole l^{-1}; λ_{irrad} = 366 nm; cell thickness = 1 cm



R	10^2k(min^{-1}) at 20° in dimethylformamide	λ_{max}(nm) in acetonitrile	6*[36]
CH_3	2·4 ± 0·08	496	0
C_2H_5	3·2 ± 0·1	492	−0·10
C_3H_7	5·0 ± 0·15	505	−0·12
n.C_8H_{17}	5·8 ± 0·25	500	
i.C_3H_7	0·67 ± 0·04	458	−0·19
$C_6H_5CH_2CH_2$	6·6 ± 0·13	518	0·08
CH_2=$CHCH_2$	12·1 ± 0·5	524	
$C_6H_5CH_2$	80·2 ± 3·0	517[a]	0·22

[a] at 15·3°

Table 5 shows that substituents with Taft's positive 6* values[36] (β-phenylethyl, allyl and benzyl) give rise to a marked increase in the rate of decolouration (a factor of about 35 with respect to Me; and also produces a bathochromic shift of λ_{max} (30 nm). However, alkylsubstituents characterized by a negative 6* (from Me to octyl) also increase the rate of decolouration, although to a much lower extent (about a twofold from methyl to n-propyl and n-octyl). Since the effect of N-alkyl-substituents on the decolouration rate is closely paralleled by that of apolar solvents

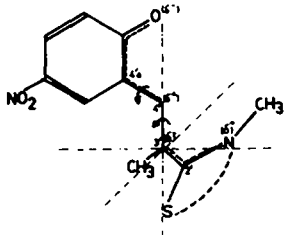
on the λ_{max} of the merocyanines (Table 1) and their rate of decolouration (Table 2) it is thought that these observations are attributable to prevention of solvation rather than to inductive effects.

In the case of the N-isopropyl compound a strong hypsochromic effect was observed as well as a decrease in rate of decolouration; examination of models shows that this peculiar behaviour can be related to the steric hindrance caused by the isopropyl group.

III. DISCUSSION

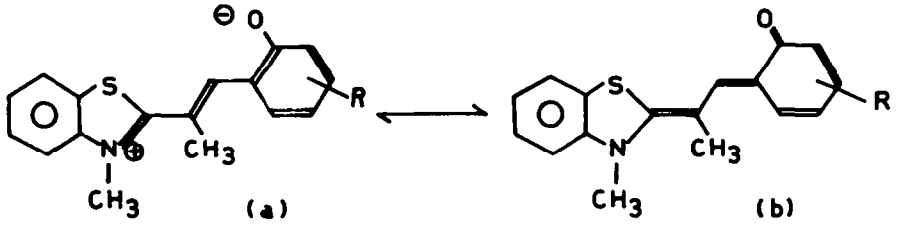
The strong solvatochromism[27–32] of the irradiated benzothiazolinospiropyrans indicates a merocyanine structure for the open form (Table 1). The hypsochromic shift of the λ_{max} of the "photomerocyanine" compared with that of the 3′-non-methylated one is due to the steric hindrance affecting the open form.[33–34]

The influence of the solvent polarity on the decolouration kinetics can be explained using figure 7.[25] Since the merocyanine exhibits a *trans* configuration with respect to the 3′–4′ bond, the ring closure necessary involves a 180° rotation of one moiety of the molecule with respect to the other one, around this 3′–4′ bond. This rotation is accompanied by another one around the 4′–4′$_a$ bond in order to permit the oxygen atom to approach the 2′ C atom.



trans—Configuration of open-merocyanine structure. Intramolecular rotation and ring closure.

In view of this fact the decolouration process will evidently be easiest when the 3′–4′ bond has a bond order close to one. A merocyanine can be represented by two



mesomeric forms, (a) and (b). While **8a** is very polar and possesses a 3′–4′ double bond, **8b** is weakly polar and possesses a 3′–4′ single bond. Any feature favouring the relative stability of the polar form, e.g. by increasing the polarity of the solvent will slow down the rate of the decolouration and increase its activation energy (Table 2).

The increase of activation entropy with the polarity of the solvent can be explained assuming that the less solvated transition state is less influenced by a variation of the solvent polarity than the merocyanine itself.

The anomalous behaviour of the 6'-nitro spiropyrans in pyridine solution is probably due to the occurrence of a solute-solvent interaction of which the nature is at present unknown.

The contribution of the mesomer (a) to the merocyanine resonance can also be increased by substitution of the negatively charged moiety of the molecule with electron withdrawing groups or, conversely, by substitution of the positive part with electron repelling groups.

Table 3 shows that an increase of the electron withdrawing character of the substituents of the benzopyran moiety markedly lowers the rate of decolouration. Although no correlation exists between the log k and the Hammett 6-constants,[35] neither with the 6^{+}[36] nor 6^{-} constants,[35] the influence of the substituents on the rate of decolouration is much more pronounced in these compounds than in the case of the indolinospiropyrans.[18]

The large hypsochromic shift of the λ_{max} (Table 3) exhibited by the 5'-methylmerocyanine is probably due to the less effective conjugation in this system resulting from non-coplanarity caused by a steric interaction between the 3' and 5'-Me groups.

Electron donor substituents in the benzothiazoline moiety increase, by inductive effect, the basicity of the ring-N atom, and thus stabilize the polar structure of the open merocyanine; consequently the rate of decolouration decreases (Table 4). This inductive effect is, as expected, much less pronounced than the effect of electron attracting substituents in the benzopyran moiety, which can contribute to the delocalization of the negative charge on this part of the molecule. In general, the activation energies of decolouration are only little affected by the introduction of substituents in the benzothiazoline moiety, except for the 6-MeO-compound, which shows an anomalously low value.

Finally, for different N-substituted merocyanines, the decolouration rate increases with an increase in electron withdrawing character of the substituents (Table 5). The anomalously low rate constant value for the N-isopropyl derivative is probably due to the steric hindrance exerted by the bulky isopropyl group. The progressive increase of the rate constant of decolouration from the N-methyl to the N-octyl derivative can be explained by a decreasing solvation effect.

Most of the experimental results described in this paper can be explained by means of a unique reaction scheme; whether the merocyanine is the only compound involved in the decoloration reaction, or whether different stereoisomers of the dye molecule are present, as in the case of the photochromism of indolinospiropyrans[11,15–17,20] and polymeric benzothiazolinospiropyrans[22] cannot be settled by these data.

IV. EXPERIMENTAL

Substituted salicylaldehydes

3- *and* 5-*Nitrosalicylaldehyde* were obtained by nitration of salicylaldehyde and separated by fractional crystallization of their sodium salts[37]. m.p.: 106–107° (3-nitro) and 125° (5-nitro). 5-*Bromosalicylaldehyde* obtained by bromination of salicylaldehyde, gives 3-*nitro* 5-*bromosalicylaldehyde* by nitration with fuming nitric acid[38], m.p. 147–148° (ethanol-benzene 1:1). Reimer–Tiemann formylation[39] of *o*-cresol, *p*-cresol, *o*-t-butylphenol, β-naphtol and thymol yielded 3- *and* 5-*cresylaldehyde*, 3-*t-butylsalicylaldehyde*,

2-hydroxy-1-naphtaldehyde[40], [m.p. 78–79° (ethanol)] and *3-isopropyl 6-cresylaldehyde*[42] respectively. 3-Cresylaldehyde, 5-cresylaldehyde, 3-t-butylsalicylaldehyde and 3-isopropyl 6-cresylaldehyde at 10°, were nitrated with fuming HNO_3 in glacial AcOH soln, and gave *5-nitro-3-cresylaldehyde*,[41] [m.p. 132–133° (EtOH)], *3-nitro-5-cresylaldehyde* [m.p. 138–141° (EtOH)], *3-isopropyl 5-nitro 6-cresylaldehyde* [b.p. 185–186° (6 mm)] and *3-t-butyl 5-nitrosalicylaldehyde* [m.p. 100–103° (EtOH)] respectively.

3,5-Dibromosalicylaldehyde[43] was obtained by bromination of salicylaldehyde. [m.p. 85–86° (EtOH 60%)]. *3,5-Diiodosalicylaldehyde*[44] was obtained by reaction of iodine and potassium iodide with salicylaldehyde, [m.p. 105–106° (EtOH)].

5-Fluorosulfonylsalicylaldehyde.[45] The reaction of chlorosulfonic acid with salicylidene aniline gave 5-chlorosulfonylsalicylidene aniline, that on treatment with KF yields 5-fluorosulfonyl-salicylidene aniline; by hydrolysis 5-fluorosulfonylsalicylaldehyde was obtained. The product was purified by steam distillation. [m.p. 120–120·5° (benzene)].

4-Chlorosalicylaldehyde[46] was prepared by Reimer-Tiemann formylation of *m*-chlorophenol.

3,5-Dibromo-4-chlorosalicylaldehyde. 20·5 g Br_2 dissolved in 75 ml glacial AcOH was added dropwise with vigorous stirring to a soln of 16 g 4-chlorosalicylaldehyde in 75 ml glacial AcOH at 40°. After 1 hr the mixture is poured onto ice. The ppt was filtered off and washed with water, yield 78%; [m.p. 122–123° (EtOH)].

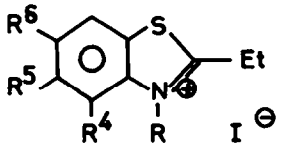
Substituted 2-ethylbenzothiazoles

2-Ethylbenzothiazole. 100 g *o*-Aminothiophenol, 110 g propionic anhydride, 8 g Zn and 26 g $ZnCl_2$ were heated at 100° for 2 hr. After neutralization with NaOH the mixture was steam distilled, yield 85%.

The synthesis of *2-ethyl-5-isobutyramidobenzothiazole* was described previously.[22]

2-Ethyl-6-methylbenzothiazole. p-Toluidine was transformed into 4-methylpropionanilide by the action of a mixture of propionic anhydride and propionic acid[47] m.p. 124–126°. 4-Methylpropionalide (78 g) was dissolved in a mixture of toluene (590 ml) and pyridine (200 ml), and the soln heated at 80°; a mixture of

TABLE 6. SYNTHESIS OF SUBSTITUTED 2-ET-3-ALKYL-BENZOTHIAZOLIUM SALTS

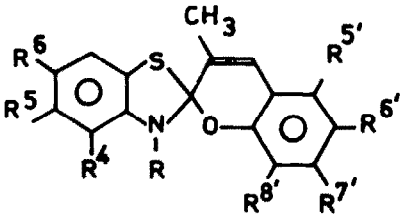


R	R^4	R^5	R^6	Solvent	M.p. (°C)[a]
CH_3	H	H	H	Benzene	182 (E) Litt. 184(49)
CH_3	H	H	CH_3	Benzene	239 (E)
CH_3	CH_3	H	H	Without	213 (E)
CH_3	H	H	CH_3	Benzene	239 (E)
CH_3	H	H	Cl	Methanol	269–270 (M-D 9/1)
CH_3	H	$(CH_3)_2CHCONH$	H	Benzene	233–234 (M-A 3/1)
C_2H_5	H	H	H	Without	193–194 (E) Litt. 194–195 (49)
$C_6H_5CH_2$	H	H	H	Without	206–207 (E)
C_3H_7	H	H	H	Without	205–206 (E)
$CH_2{=}CH{-}CH_2$	H	H	H	Without	125–126 (E)
i.C_3H_7	H	H	H	Without	205–220 (b) Litt. 172 (49)
$C_6H_5CH_2CH_2$	H	H	H	Without	177–180 (E-B 1/1)
n.C_8H_{17}	H	H	H	Without	*b*

[a] m.ps are not corrected; E = ethanol, M = methanol, D = dimethylformamide, A = acetone, B = benzene.

[b] compounds used without further purification.

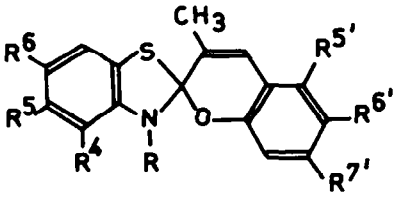
TABLE 7



R	R^4	R^5	R^6	$R^{5'}$	$R^{6'}$	$R^{7'}$	$R^{8'}$	Yield %[a]	m.p. [b]	Formula	Analyses % Calc C	Calc H	Calc N	Calc O	Calc S	Found C	Found H	Found N	Found O	Found S
CH_3	CH_3	H	H	H	NO_2	H	H	11	166·5–167·5	$C_{18}H_{16}N_2O_3S$	63·5	4·7	8·23	14·10	9·42	63·7	4·8	8·12	14·19	9·34
CH_3	H	H	CH_3	H	NO_2	H	H	30	166	$C_{18}H_{16}N_2O_3S$	63·5	4·7	8·23	14·1	9·42	63·95	4·7	8·19	14·42	9·46
CH_3	H	H	CH_3O	H	NO_2	H	H	30	162–163 (Litt. 157–158)	$C_{18}H_{16}N_2O_4S$	60·7	4·5				60·8	4·8			
CH_3	H	H	Cl	H	NO_2	H	H	38	182–183	$C_{17}H_{13}ClN_2O_3S$[e]	56·6	3·6	7·76	13·30	8·89	56·2	3·6	7·61	12·83	8·68
C_2H_5	H	H	H	H	NO_2	H	H		146–147 (Litt. 152)	$C_{18}H_{16}N_2O_3S$	63·5	4·7	8·23	14·1	9·42	63·4	4·7	8·29	14·09	9·51
C_3H_7	H	H	H	H	NO_2	H	H		174·5–175·5	$C_{19}H_{18}N_2O_3S$	64·4	5·1	7·90	13·54	9·05	64·5	5·1	7·73	13·30	9·01
iC_3H_7	H	H	H	H	NO_2	H	H		165–167	$C_{19}H_{18}N_2O_3S$	64·4	5·1				64·2	5·1			
nC_8H_{17}	H	H	H	H	NO_2	H	H		90–91·5 (EB 4/1)	$C_{24}H_{28}N_2O_3S$	67·9	6·6	6·6	11·31	7·55	67·4	6·5	6·54	11·11	7·37
$CH_2{=}CH{-}CH_2$	H	H	H	H	NO_2	H	H		166–168 (EB 2/1)	$C_{19}H_{16}N_2O_3S$	64·8	4·6	7·95	13·62	9·10	64·9	4·6	7·77	13·40	9·59
$C_6H_5CH_2$	H	H	H	H	NO_2	H	H		186 (EB 7/3)	$C_{23}H_{19}N_2O_3S$	68·5	4·8	6·95	11·9	7·95	68·26	4·3	7·03	11·8	7·82
$C_6H_5CH_2CH_2$	H	H	H	H	NO_2	H	H		158–159 (EB 4/1)	$C_{24}H_{21}O_3S$	69·0	5·1	6·71	11·50	7·68	68·9	4·7	6·52	11·02	7·54
CH_3	H	H	H	H	Br	Cl	Br		87–88	$C_{17}H_{12}Br_2ClNOS$	43·1	2·5	2·96	3·38	6·77	43·0	2·7	2·77	3·13	6·44
CH_3	H	H	H	H	H	H	NO_2		184–185 (Litt. 186–187)	$C_{17}H_{14}N_2O_3S$	62·5	4·3	8·6	14·71	9·82	62·4	4·4	8·6	14·47	9·76
CH_3	H	H	H	H	Br	H	NO_2	9	182·5–183	$C_{17}H_{13}BrN_2O_3S$	50·4	3·2	6·9	11·8	7·9	50·4	3·2	6·9	11·6	7·8
CH_3	H	H	H	CH_3	NO_2	H	iC_3H_7	24	152–153·5	$C_{21}H_{22}N_2O_3S$	65·9	5·8	7·3	12·5	8·4	65·7	5·9	7·2	12·5	8·5
CH_3	H	H	H	H	Br	H	Br	82	142–144 (EB 4/1)	$C_{17}H_{13}Br_2NOS$[e]	46·49	2·98	3·19	3·64	7·30	45·75	3·05	3·17	3·53	6·97
CH_3	H	H	H	H	I	H	I	88	146–148 (EB 4/1)	$C_{17}H_{13}I_2NOS$‖	38·29	2·46	2·63	3·00	6·01	37·69	2·55	2·46	2·93	5·77
CH_3	H	iba[g]	H	H	NO_2	H	H		230–232	$C_{21}H_{21}N_3O_4S$	61·3	5·14	10·2	15·55	7·8	60·62	5·34	10·1	15·61	7·6
CH_3	H	H	H	H	NO_2	H	H	42	157 (Litt. 158–159)	$C_{17}H_{14}N_2O_3S$	62·58	4·32	8·58	14·71	9·8	63·36	4·62	8·40	14·18	9·54
CH_3	H	H	H	H	NO_2	H	CH_3	68	177·5–178·5 (EB4/1)	$C_{18}H_{16}N_2O_3S$	63·51	4·74	8·23	14·10	9·4	63·20	4·92	8·37	14·27	9·4
CH_3	H	H	H	H	CH_3	H	NO_2	95	182–182·5	$C_{18}H_{16}N_2O_3S$	63·51	4·74	8·23	14·10	9·4	63·40	4·88	8·38	14·2	9·4
CH_3	H	H	H	H	NO_2	H	tC_4H_9		195–196 (EB 7/3)	$C_{20}H_{20}N_2O_3S$	65·19	5·47	7·60	13·03	8·7	64·97	5·68	7·51	12·86	8·6
CH_3	CH_3	H	H	H	NO_2	H	tC_4H_9		186–189 (EB 7/3)	$C_{21}H_{22}N_2O_3S$	65·94	5·80	7·32	12·55	8·4	66·16	6·02	7·08	12·13	8·3
CH_3	H	H	H	H	SO_2F	H	H		147–148	$C_{17}H_{14}FNO_3S_2$	56·18	3·88	3·85	13·21	17·6	56·14	3·94	4·10		17·4

[a] Calc. Br: 36·4; Found Br: 36·2;
‖ Calc. 1: 47·8; Found 1: 47·9.
‖ Calc. 1: 47·18; Found 1: 47·9.
[c] After crystallization.
[b] The m.ps are not corrected. Recrystallization solvent: ethanol–benzene 1/1 unless otherwise indicated. EB = ethanol–benzene; H = heptane;
[f] The reaction solvent was acetonitrile.
[d] The reaction mixture may not be heated.
[g] iba = isobutyramido.

TABLE 8. NMR SPECTRA OF SPIROPYRANS



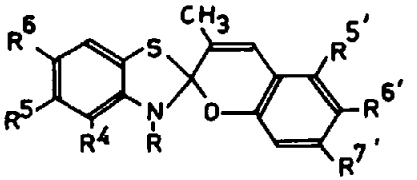
R	R^4	R^5	R^6	$R^{5'}$	$R^{6'}$	$R^{7'}$	$R^{8'}$	Position of the peaks (τ) (multiplicity)[a]			
								3'-CH_3	3-CH_3	4'H	Other peaks
CH_3	H	H	H	H	NO_2	H	H	7·90(d)	6·97(s)	3·39(q)	
CH_3	H	H	H	H	Br	H	NO_2	7·90(d)	6·95(s)	3·41(q)	
CH_3	H	H	H	Benzo		H	H	7·89(d)	6·95(s)		
CH_3	H	iba	H	H	NO_2	H	H	7·91(d)	6·97(s)		
CH_3	H	H	H	H	I	H	I	7·97(d)	6·99(s)		
CH_3	H	H	H	H	CH_3	H	NO_2	7·92(d)	7·00(s)		6'-CH_3: 7·70
CH_3	H	H	H	CH_3	NO_2	H	i.C_3H_7	7·90(d)	6·96(s)		methyl groups in i.C_3H_7: 8·77 and 8·99
CH_3	H	H	H	H	NO_2	H	t.C_4H_9	7·90(d)	6·95(s)	3·40(q)	8'-t.C_4H_9: 8·80(s)
CH_3	CH_3	H	H	H	NO_2	H	t.C_4H_9	7·91(d)	6·65(s)	3·40(q)	4-CH_3: 7·39; 8'-t.C_4H_9: 8·77(s)
CH_3	H	H	H	H	H	H	NO_2	7·94(d)	6·94(s)	3·40(q)	
CH_3	H	H	H	H	Br	Cl	Br	7·91(d)	6·97(s)		
C_2H_5	H	H	H	H	NO_2	H	H	7·91(d)		3·36(q)	3-$\underline{CH_2}$—CH_3: 6·46(m); 3-CH_2—$\underline{CH_3}$: 8·65(t)

TABLE 8—*continued*

R	R^4	R^5	R^6	$R^{5'}$	$R^{6'}$	$R^{7'}$	$R^{8'}$	Position of the peaks (τ) (multiplicity)			
								3'-CH_3	3-CH_3	4'H	Other peaks
C_3H_7	H	H	H	H	NO_2	H	H	7·92(d)		3·40(q)	3-$\underline{CH_2}$—CH_2—CH_3: 6·63; 3-CH_2—$\underline{CH_2}$—$\underline{CH_3}$: 8·25; 3-CH_2—CH_2—$\underline{CH_3}$: 9·06(t)
i.C_3H_7	H	H	H	H	NO_2	H	H	7·88(d)		3·38(q)	methyl groups in 3-i.C_3H_7: 8·40(d) and 8·50(d) 3-$\underline{CH}(CH_3)_2$: 6·12
n.C_8H_{17}	H	H	H	H	NO_2	H	H	7·90(d)		3·38(q)	-$(\underline{CH_2})_6$—CH_3; 8·71; $(CH_2)_7$—$\underline{CH_3}$: 9·09(t) $\underline{CH_3}$—$(CH_2)_6$—CH_3: 6·65
CH_2═CH—CH_2	H	H	H	H	NO_2	H	H	7·90(d)		3·38(q)	$\underline{CH_2}$—CH═CH_2: 5·91; CH_2—$\underline{CH}$═CH_2: 4·20; CH_2—CH═$\underline{CH_2}$: 4·73
$C_6H_5CH_2$	H	H	H	H	NO_2	H	H	7·90(d)			$\underline{CH_2}$—C_6H_5: 5·29(d); CH_2—$\underline{C_6H_5}$: 2·69(s)
$C_6H_5CH_2CH_2$	H	H	H	H	NO_2	H	H	7·96(d)		3·38(q)	$\underline{CH_2}$—CH_2—C_6H_5: 6·89; CH_2—$\underline{CH_2}$—C_6H_5: 6·38; $(CH_2)_2$—$\underline{C_6H_5}$: 2·84
CH_3	CH_3	H	H	H	NO_2	H	H	7·90(d)	6·67(s)	3·40(q)	4-CH_3: 7·40
CH_3	H	H	CH_3	H	NO_2	H	H	7·92(d)	7·00(s)		6-CH_3: 7·70
CH_3	H	H	Cl	H	NO_2	H	H	7·92(d)	6·99(s)		

[a] solvent: $CDCl_3$; s = singlet; d = doublet; q = quadruplet; m = multiplet

TABLE 9. UV SPECTRA OF SPIROPYRANS IN DIMETHOXYETHANE



R	R^4	R^5	R^6	$R^{5'}$	$R^{6'}$	$R^{7'}$	$R^{8'}$	λ_{max} (mμ)/log ε[a]			
CH_3	H	H	H	H	NO_2	H	H	(253)	269 4·45	303 4·14	(336)
CH_3	CH_3	H	H	H	NO_2	H	H		266 4·38	303 4·00	(333)
CH_3	H	H	CH_3	H	NO_2	H	H		268 4·36	307 4·05	(336)
CH_3	H	H	CH_3O	H	NO_2	H	H	226 4·53	268 4·33	318 4·05	(350)
CH_3	H	H	Cl	H	NO_2	H	H	229 4·60	266 4·42	312 4·06	(340)
CH_3	H	iba	H	H	NO_2	H	H	232 4·65	268 4·55	311 4·22	(341)
CH_3	H	ma	H	H	NO_2	H	H	(235)	269 4·47	319 4·28	
C_2H_5	H	H	H	H	NO_2	H	H	(245)	269 4·39	303 4·05	(333)
C_3H_7	H	H	H	H	NO_2	H	H	(253)	269 4·33	303 4·00	(338)
$i.C_3H_7$	H	H	H	H	NO_2	H	H	(254)	268 4·34	303 4·01	(334)
$n.C_8H_{17}$	H	H	H	H	NO_2	H	H	(251)	268 4·40	303 4·08	(334)
$CH_2^{\circ}=CH-CH_2$	H	H	H	H	NO_2	H	H	(253)	267 4·36	300 4·03	(335)
$C_6H_5CH_2$	H	H	H	H	NO_2	H	H	(254)	269 4·32	(299)	(332)
$C_6H_5CH_2CH_2$	H	H	H	H	NO_2	H	H	254 4·35	267 4·35	301 4·02	(336)

TABLE 9—*continued*

R	R^4	R^5	R^6	$R^{5'}$	$R^{6'}$	$R^{7'}$	$R^{8'}$	λ_{max} (mμ) log ε^a							
CH_3					NO_2		CH_3		250 4·38	272 4·32		(302)		(335)	
CH_3					NO_2		$t.C_4H_9$	(227)	(246)	272 4·31		(302)		(343)	
CH_3				CH_3	NO_2		$i.C_3H_7$		260 4·32	(268)		(303)			(360)
CH_3					CH_3		NO_2		(253)			(292)		348 3·52	
CH_3							NO_2		(249)			(291)		338 3·55	
CH_3					Br		NO_2		(248)	273 4·39		(302)	(322)		
CH_3					Br		Br	237 4·70		272 4·01	283 3·97	303 3·82	(330)		
CH_3					I		I		246 4·88	275 4·22	285 4·19	(304)	(326)		
CH_3					Br	Cl	Br	240 4·46		279 4·07		290 4·08	324 3·56		
CH_3					SO_2F							300 4·00			
CH_3			Benzo								(290)	303 4·11	316 4·02	342 3·80	357 3·79

[a] (λ) = shoulder bands

P_2S_5 (118 g) and K_2S (72 g) was added slowly (1 hr); after addition, the mixture was stirred for 3 hr at 120°. The liquid was decanted and the solid residue extracted 3 times with a mixture of toluene (80 ml) and pyridine (30 ml). The extracts were added to the decanted liquid and the soln evaporated to dryness under reduced press. The residue of 4-methyl-thiopropionalide (22·2 g) was dissolved in NaOH aq (250 ml, 8% w/w). The resulting soln was added dropwise to an aqueous soln of potassium ferricyanide (500 ml, 25% w/w). After addition the mixture was stirred for 3 hr while the temp was maintained 5°. The 2-ethyl-6-methylbenzothiazole[48] was extracted with ether and distilled, yield 53%; b.p. 96–98° (0·6 mm).

2-Ethyl-4-methylbenzothiazole. This material was prepared as described above, but starting from *o*-toluidine [(2-methyl propionanilide: m.p. 88–89°; 2-ethyl-4-methylbenzothiazole: b.p. 112–114° (5 mm)].

2-Ethyl-6-methoxybenzothiazole. Prepared from *p*-anisidine: [(4-methoxypropionanilide: m.p. 91–92°; 2-ethyl-6-methoxybenzothiazole: b.p. 138–141° (0·7 mm)].

2-Ethyl-6-chlorobenzothiazole. Prepared starting from *p*-chloroaniline: [(4-chloropropionanilide: m.p. 137–138°; 2-ethyl-6-chlorobenzothiazole: b.p. 113–115° (0·6 mm)].

2-Ethyl 3-alkylbenzothiazolium iodides

These salts are readily obtained by heating the benzothiazole with an excess of alkyl iodide in a sealed tube at 80°. The reaction rate is strongly dependent on the structure of both reactants.

Table 4 gives the synthetic process used to obtain the quaternary salts.

Spiropyrans

To avoid repetition, one example of spiropyran synthesis is given.

Quaternary salt (0·01 mole) and a substituted salicylaldehyde (0·01 mole) were heated in MeOH (10 ml), in the presence of piperidine (1 ml); the spiropyran precipitated on cooling and was recrystallized. Its degree of purity was determined by elemental analysis.

The analyses, m. ps, NMR and UV spectra of the spiropyrans are given in Tables 7, 8 and 9, respectively.

Solvents

Methanol, isopropanol, acetone, methylene chloride and dioxan were spectroscopic grade solvents (Merck). Chlorobenzene was a chromatography grade solvent (UCB). Abs ethanol, acetonitrile and butanone were A.R. grade products (UCB). Chloroform: A.R. grade (Merck). Tetrahydrofuran, toluene (A.R. grade, UCB) and dimethoxyethane (Fluka purum) were fractionated from Na wire and pyridine (A.R. grade UCB) from KOH, immediately before use. Dimethylformamide (A.R. grade UCB) was refluxed for 1 hr in presence of 10% MeOH (A.R. grade UCB). The mixture was then fractionated.

Spectrophotometric techniques

The visible and UV absorption spectra were determined with a Cary Model 14 Spectrophotometer.

Kinetic measurements were carried out in the following way: the thermostated solns were irradiated outside the spectrophotometer with a 180 W Hanau lamp, using Iena interference filters to obtain either 313 or 366 nm monochromatic light. Otherwise a potassium biphtalate soln (5 g/L) was used to cut off light of wavelength below 300 nm. When the desired merocyanine concentration was attained, the cell was transferred to the spectrophotometer or to an Eppendorf colorimeter.

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