Structure of rhodanine cyanine dyes, spectroscopy and performance in photographic emulsions

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The synthesis is reported of eight pyridine-, benzothiazole- and benzimidazole-rhodanine zeromethine merocyanines as bluesensitising dyes (1-8), and of three benzoxazole-rhodanine dimethine merocyanines as green-sensitising dyes (9-11). The compounds were characterised from UV-VIS, mass spectroscopic and NMR data, and the purity of the products was analysed using HPLC. Oxidation potentials were measured using cyclic voltammetry. Ionisation potentials and electron affinities were obtained by semi-empirical MOPAC calculations. The charge-density distributions of the pyridine and benzothiazole rhodanine dyes are in agreement with assignments in NMR spectroscopy. A linear dependence is found between the oxidation potential and ionisation potential, as well as between the reduction potential and electron affinity. Reflection spectra of 6 and 7 coated on photographic emulsions showed J-aggregate absorption at $\lambda = 450$ and 465 nm, respectively. The sensitising properties of the merocyanine dyes were evaluated in actual photographic T-grain emulsions.

Silver halide crystals, which constitute the sensitive elements in most photographic processes, have significant sensitivity only to the ultraviolet, violet and blue region of the spectrum, while the human eye is sensitive to the part of the electromagnetic spectrum between $\lambda = 400$ and 700 nm. Since silver halide emulsions are unaffected by green, yellow, orange and red light, these 'colour-blind' materials give photographs in which the tone values are distorted and therefore cannot be used as the basis for colour photography. The sensitivity of silver halide must be extended from $\lambda = 480$ nm (blue light) into the $\lambda = 500-600$ nm (green light) and 600-700 nm (red light) regions of the visible spectrum in order to produce colour photographic products.

Rhodanine merocyanine dyes are well known as sensitising dyes in photographic emulsions.¹⁻⁶ In a continuation of our research programme on functional dyes,⁷⁻⁹ three pyridinerhodanine zeromethine merocyanines (1-3), four benzothiazole-rhodanine zeromethine merocyanines (4-7), and one benzimidazole-rhodanine zeromethine merocyanine dye (8) were synthesized and their efficiencies tested as blue sensitizers in photographic T-grain emulsions. The formulae of the compounds are shown in Fig. 1(a)-(d). Three benzoxazole-rhodanine dimethine merocyanine dyes (9-11) were also synthesized and their efficiencies tested as green sensitizers. The formulae of these compounds are given in Fig. 1(e)-(f). High-pressure liquid chromatography (HPLC) was used to check the purity of the compounds. Chemical ionization mass spectroscopy proved efficient to confirm the empirical formula and purity of the merocyanine compounds. Fast atom bombardment mass spectrometry (FAB MS) proved useful to check the structure of selected dyes and intermediates. The compounds were further characterized by UV-VIS spectroscopy and NMR measurements. The structures of the zeromethine dyes were also studied by semi-empirical MOPAC 93 calculations, and the charge distributions correlated with the NMR spectra. The ionization potentials and electron affinities were related to the one-electron reduction and the one-electron oxidation potentials measured by cyclic voltammetry. These properties were then correlated with dye solubility, sensitizing efficiency and dyeing extent (residual dye density).

Experimental

Syntheses

N-Methyl-2-thiomethyl pyridinium iodide¹⁰ (QL1). 2-Sulfanylpyridine (5 g, 0.045 mol) and NaHCO₃ (5.67 g, 0.06 mol) were suspended in 20 ml water, then dimethyl sulfate (13 ml, 0.137 mol) was added dropwise over a period of about 20 min to the solution while stirring vigorously. The solution was stirred at 20-25 °C for a further 100 h. Sodium iodide (16 g) was added to the solution which was cooled in an ice bath. Orange needles of the crude product were precipitated. After filtration, the product was washed with diethyl ether and acetone, and then crystallized from ethanol. Yellow crystals, mp 140–142 °C. Yield 50%.

1,3-Dimethyl-2-thiomethyl-3H-benzimidazolium iodide¹⁰ (QL6). 1,3-Dimethyl-2-thiomethyl benzimidazolium iodide (QL6) was prepared similarly to QL1, but using 2-sulfanylbenzimidazole (7.5 g, 0.05 mol), NaHCO₃ (12.6 g, 0.06 mol) and dimethyl sulfate (23.7 ml, 0.25 mol). A yellow powder was obtained with mp 138–140 °C. Yield 51%.

The other QL salts were synthesized under the conditions reported in our recent work,⁹ some details are given in Table 1.

N-Methyl-2-[(3-ethyl-4-oxo-2-thioxo-1,3-thiazolidin-5ylidene)]pyridine (1). *N*-Methyl-2-thiomethyl pyridinium iodide, QL1 (1 g, 0.00375 mol) and *N*-ethyl rhodanine (0.6 g, 0.00375 mol) were dissolved in 10 ml water-free alcohol and the solution was heated to 80 °C, triethylamine (1 ml, 0.007 mol) was added and the mixture heated at reflux under an N₂ atmosphere for 45 min. The solution was then cooled in a refrigerator overnight. The precipitate was filtered and washed with a mixture of acetone and diethyl ether (1:1), and



Fig. 1 Formulae and numbering used for the compounds, together with atomic numbering schemes

Table 1 Synthetic details of QL quarternary salts [see Fig. 1(g) for formulae]

	mp/°C		reaction conditions		
		yield (%)	T/°C	t/h	
OL1	140–142	50	25	100	
ÕL2	125-126	24	see ref. 9)	
Òl3	221-223	99	see ref. 9)	
Òl4	142-144	30	see ref. 9)	
ÒL5	117-120	30	see ref. 9)	
QL6	138-140	51	25	100	

then recrystallized three times from ethanol and 0.5 g final red product was obtained; mp 152–153 °C; yield 56%.

The other blue-sensitizing dyes (2-8) were synthesized under similar conditions to the one described above.

2-Methyl-3-ethyl-5-phenyl-1*H*-benzoxazolium iodide (QM1). A mixture of 2-methyl-5-phenylbenzoxazole (11 g, 0.053 mol) and ethyl iodide (11 ml, 0.075 mol) was heated under a nitrogen atmosphere on an oil bath to $120 \,^{\circ}$ C for 12 h. Large amounts of solid products were formed during the reaction. Upon cooling to room temperature, acetone was added to wash the crude products, which were crystallized from ethanol. The white product (9 g; 53%) was dried in vacuum, mp 190–192 °C. 2-[2-(N-Acetylanilino)ethenyl]-3-ethyl-5-phenyl-1H-benzoxazolium iodide (QM4). A mixture of 2-methyl-3-ethyl-5phenylbenzoxazolium iodide (3.66 g, 0.01 mol) and N,N'diphenylformamidine (5.88 g, 0.03 mol) was heated under a nitrogen atmosphere on a metal bath to 160 °C for 1 h. During the reaction a vacuum of about 1 mmHg was maintained to distill off the byproduct aniline. Upon cooling to room temperature, acetic anhydride (20 ml) was added and the mixture heated at reflux at 140 °C for 1 h. After distillation of the solvent, acetone (40 ml) was added and the the mixture was heated to reflux. Finally, 70 ml diethyl ether was added to precipitate the product. The solution was kept in the refrigerator overnight. A dark red product (2.4 g) was obtained, and dried in vacuum. Yield 47%; mp 278-280 °C.

5-Methoxy-2-methyl-3-(4-sulfonatobutyl)-1*H*-benzoxazolium (QM2). A mixture of 4.1 g (0.025 mol) of 5-methoxy-2methyl-1*H*-benzoxazole and 3.7 g (0.03 mol) of 1,4-butanesulfone (1,2-oxathiane-2,2-dioxide) was gradually heated to 120 °C and kept at this temperature for 22 h, during which time the colour changed from yellow to dark brown. After cooling, the product was filtered, washed with a mixture of cold acetone and methanol (1:1, v/v), and crystallized from methanol; mp 258-260 °C, yield 3.6 g (48%).

2-{2-(N-Acetylanilino)ethenyl}-5-methoxy-3-(4-sulfonatobutyl)-1H-benzoxazolium (QM5). A mixture of 5-methoxy-2-methyl-3-(4-sulfonatobutyl)-1H-benzoxazolium (QM2) (3.0 g, 0.01 mol) and N,N'-diphenylformamidine (5.88 g, 0.03 mol) was heated under a nitrogen atmosphere at 140 °C for 1 h. During the reaction, a vacuum of about 1 mmHg was maintained to distill off the byproduct aniline. Upon cooling to room temperature, acetic anhydride (10 ml) was added and the mixture was heated at reflux at 140 °C for 1 h. After distillation of the solvent, 40 ml acetone was added and the mixture was heated at reflux for 1 h. Finally, 70 ml diethyl ether was added to precipitate the product. The solution was kept in a refrigerator overnight; mp 296–298 °C, yield 1.6 g (35%).

QM3 was prepared in the same way as QM2, starting from 5-chloro-2-methyl-1*H*-benzoxazole. QM6 was synthesized following the procedure described for QM5, starting from QM3. Synthetic details of all QM compounds used are collected in Table 2.

N-Ethyl-5-phenyl-2-[2'-(3-ethyl-4-oxo-2-thioxo-1,3-thiazolidin-5-ylidene)ethenyl]-1*H*-benzoxazole (g). In 10 ml acetic anhydride, a mixture of 5-phenyl-3-ethyl-2-(2'-*N*-acetanilinoethenyl)benzoxazolium iodide (0.5 g, 0.001 mol) and *N*-ethyl rhodanine (0.16 g, 0.001 mol) was heated to 140 °C on an oil bath for 1 h in the presence of a tertiary amine (NEt₃). Upon cooling, 50 ml ice was added to precipitate the products. After recrystallisation three times from methanol, 0.1 g of red, needlelike crystals was obtained. Yield 25%, mp 220-222 °C.

Compounds 10 and 11 were synthesized similarly. Equimolar amounts of the ICI intermediate compound and *N*-ethyl rhodanine were reacted using the same conditions as described

 Table 2 Synthetic details of QM quarternary salts [see Fig. 1(h) and
 (i) for formulae]

	mp/°C	yıeld (%)	reaction conditions		
			<i>T</i> /°C	t/h	
OM1	190–192	53	120	12	
ÒМ2	258-260	48	120	22	
ÒМ3	278-280	76	140	24	
ÒM4	278-280	47	140	1	
о̀м5	296-298	35	140	1	
QM6	285-287	50	140	1	

above. The crude dye was precipitated with a cold NaI solution and purified with vacuum liquid chromatography at a pressure of 10–20 mmHg, using silica gel (type H, TLC grade, particle size 10–40 mm) as the sorbent, and eluting with butanol-acetic acid-H₂O (4:1:5 vvv).

Mass spectra

Direct probe chemical ionization (DCI) spectra of the dyes 1-8 were recorded on a RIBER-1-10B mass spectrometer equipped with a SIDAR DATA system. Compounds were dissolved and placed on a 60 μ m tungsten filament with the aid of a micro-syringe. After evaporation of the solvent, the DCI probe was inserted in the NH₃ reagent gas, and the wire was heated at a rate of 9 mA s⁻¹ until ions were observed. Primary ionisation of the reagent gas (NH₃) was achieved with the aid of 70 eV electrons. The ionisation current was 0.08 mA and the source temperature was 150 °C. The pressure in the ion source was 0.1 Torr. The DCI spectra of the zeromethine dyes showed in all cases the molecular ion peak [M+H]⁺, proving the correctness of the empirical formula. With the exception of the spectra of **6** and **8**, no spurious peaks indicative of impurities were noted.

Fast atom bombardment (FAB) mass spectra of selected intermediates and dyes were obtained on a Finnigan TSQ 70 mass spectrometer equipped with an ION TECH FAB gun operating at 8 kV on xenon. Positive-ion FAB mass spectra were recorded and controlled by the Finnigan data system by repetitive scanning over the range m/z = 50-1000 with a scan rate of 1 s. The products were mixed with trifluoracetic acidglycerol prior to analysis.

NMR Measurements

¹H and ¹³C NMR spectra of compounds in deuteriated dimethyl sulfoxide solution or deuteriated methanol solution were recorded at 30 °C on a JEOL FX 100 spectrometer. A Varian Unity spectrometer operating at 400 MHz for protons and at 100 MHz for carbons, respectively, was used in conjunction with a Sun Spark (Palo Alto, CA) data system. Tetramethylsilane was used as the internal standard. The atomic numbering schemes of the rhodanine dyes are shown in Fig. 1.

UV-VIS and reflection spectra

UV-VIS spectra were recorded at room temperature on an UV-8415A spectrophotometer. The absorption spectra of the dyes were determined from methanol solutions (dye concentration *ca.* 5×10^{-6} mol l⁻¹).

Reflection spectra were recorded at room temperature on a Hitachi 557 UV-VIS reflection spectrometer. Coated Ag^IBr T-grain emulsions without dyes were used as reference.

MOPAC calculations and electrochemical measurements

Since no experimental geometries are available for most of the rhodanine dyes, we used the semi-empirical MOPAC 93 package in the PM3 approach to calculate the geometries of some blue-sensitizing dyes. The geometries were fully optimised without any constraints. In case different configurations around the C(2)=C(5') bond are possible, the configuration of lowest calculated energy was used in the further analyses. (The *E* configuration calculated for **5** is supported by a single-crystal X-ray determination.¹⁶)

Oxidation potentials (E_{ox}) were measured using a Princeton Applied Research Corp. EG&G PARC model 175 potentiostat in conjunction with a Universal Program, EG&G PARC 174A Polarographic Analyser. The scanning speeds were 100 and 200 mV s⁻¹ and the sensitivities were 0.1 and 0.2 mA cm⁻¹. The working electrode was a Pt disk of area *ca*. 0.1 cm². Cyclic voltammetry curves of the dyes were recorded on a EG&G PARC RE 0074 X-Y recorder All potentials were measured vs the NaCl saturated calomel electrode (SCE)

Photographic emulsions

The tabular grain emulsion was precipitated using the doublejet method with automated control of pAg It was then coagulated, washed, redispersed and chemically sensitized with S+Au sensitizers, spectrally sensitized with 1–11 at various concentrations, coated on the base, and finally dried Film strips were exposed using a tungsten lamp (5500 K), and exposure times stepped up with 1/20 s employing a Xang Fong (Shanghai, P R China) exposure meter The strips were developed in D-19 b developer for 5 min at 20 °C, followed by fixation in F-5 fixer for 40 min Density, fog and maximum density of the dried films were measured Transmission densities were used to construct the characteristic curve from which sensitivity (speed) and contrast followed ¹⁷

Results and Discussion

Syntheses

The zeromethine merocyanines (blue-sensitizing dyes) 1-8 were prepared by the reaction of *N*-ethyl rhodanine (*N*-ethyl-2-



Scheme 1 Synthetic route towards 1

thioxo-4-thiazolidinone) with a heterocyclic quaternary salt carrying in the 2-position a thioalkyl leaving group [QL salts, Fig 1(g)] Scheme 1 gives as an example the steps in the preparation of 1 Starting from 2-sulfanylpyridine, the quaternization at N and the formation of the thioether function are best performed in a single step. The one-step synthesis leads to better homogeneity of the intermediate QL salts as we observed previously⁹ It also means that when diethyl sulfate is used to produce N-C₂H₅ (as for 2), or 1,4-butanesultone to produce N-(CH₂)₄SO₃⁻ (as for 4), the QL intermediate contains S-C₂H₅ and S-(CH₂)₄SO₃⁻, respectively, which fortunately are as good leaving groups as SCH₃

The final step towards the merocyanine dyes was carried out in alcohol or acetic anhydride solution in the presence of a tertiary amine $[eg N(C_2H_5)_3]$ The products were recrystallized two or three times from alcohol or acetic acid

The dimethine merocyanines (green-synsitizing dyes) 9–11, were prepared by a multi-stage reaction First, the appropriate heterocyclic compound carrying an active methyl group in the 2-position was quaternized at N The resulting salt [QM1–QM3, Fig 1(h] was then reacted with diphenylformamidine to produce the corresponding intermediate, an anilidovinyl compound [often called ICI intermediate, QM4–QM6, Fig 1(i)] Then, the ICI intermediate was acylated in acetic anhydride to obtain more reactivity Finally, the acylated ICI intermediate was reacted with N-ethylrhodanine in the presence of a tertiary amine to obtain the final dimethine merocyanine dye Details regarding the synthesis of 9 are depicted in Scheme 2, and are described later

To check the purity, compounds 1–11 were analysed by HPLC, using a Lichropep 25-40 RP 18 column, and CH₃OH-H₂O (2 1 v/v) as eluent at a flow rate of 10 ml min⁻¹ at 3500 psi pressure A Waters Associates Model 440 UV detector was employed, operating at 214 nm Retention times, yields, melting points and calculated purities are given in Table 3 The elemental analyses of some dyes are shown in Table 4 In the cases of 1 and 5 a capillary electropherogram was made, giving a purity of 100%, thus confirming the result obtained from HPLC The experiment was performed on a



Scheme 2 Synthetic route towards 9

Table 3 Yields after purification, resulting melting points, purity from HPLC [using CH_3OH-H_2O (2:1) as eluents] and retention times of 1-11 (see Fig. 1 for numbering of compounds)

dye	yield (%)	mp/°C	purity (%)	retention time/min
1	56	152-153	99	12.0 ^a
2	42	148-149	100	3.7
3	60	220-222	100	3.2
4	28	249-252	100	4.4
5	63	244-245	98	4.2
6	65	280-282	85	4.6
7	50	311-313	90	4.2
8	52	228-230	85	3.2
9	25	220-222	95	8.8
10	43	218-220	90	8.1
11	51	> 300	86	8.5

^{*a*}Eluted with CH₃OH-H₂O = 50: 50 (v/v).

 Table 4 Elemental analyses of some dyes (see Fig. 1 for numbering of the compounds)

dye		e	expt. (%)			calc. (%)		
	formula	N	С	Н	N	С	Н	
1 2 3 4 9	$\begin{array}{c} C_{11}H_{12}N_2OS_2\\ C_{12}H_{14}N_2OS_2\\ C_{11}H_{10}N_2O_3S_2\\ C_{22}H_{31}N_2O_6S_4\\ C_{22}H_{20}O_2N_2S_2 \end{array}$	10.77 10.33 9.14 7.39 6.78	51.81 53.57 44.66 46.60 64.75	3.92 5.00 3.53 5.60 4.96	11.11 10.53 9.93 7.49 6.86	52.38 54.14 46.81 47.06 64.71	4.76 5.26 3.55 5.53 4.90	

Waters Quanta 4000 CE system, applying a 20 kV electric field, and using a sodium phosphate buffer solution at pH=7. The retention time of 1 was 10.5 min, and that of 5 was 11.0 min. The retention times are in agreement with the neutral character of the compounds.

Mass spectra

pyridine-alkyl side chain

rhodanine-alkyl side chain

rhodanine moiety

FAB mass spectra of intermediate QL1 showed the molecular ion M⁺ at m/z = 140, the cluster ion $[MI+M]^+$ at m/z = 407, and the loss of CH₃ from M⁺ at m/z = 125. The tandem mass spectra (MS/MS) of the ion at m/z = 407 and the parent spectra of the ions at m/z = 125 and 140 showed the same fragmentation as the direct FAB mass spectra. FAB mass spectra of QL6 indicated: M⁺ at m/z = 193, the loss of CH₃ from M⁺ at m/z =178. MS/MS spectra of the ion at m/z = 193 showed the loss of CH₃ and SCH₃ groups.

The molecular masses of 3 and 4 were confirmed again from the FAB mass spectra. Moreover, MS/MS experiments on

H(5)

H(6)

CH₂

CH3

CH₂

CH₃

7.68

8.55

4.02

4.03

1.14

their molecular ions showed that they fragment by losing HCOOH and $SC(=S)NCH_2COOH$.

Turning to the green-sensitizing dyes, the FAB mass spectrum of 11 showed the molecular ion of the intact dye cation (M^+) at m/z=474, and also revealed the cluster ions $[M+Na]^+$ and $[M+2Na]^+$ at m/z=497 and 520, respectively. Furthermore, it showed the loss of sulfur and of H₂SO₃, thus confirming the main features of the molecular structure.

Finally, the FAB mass spectra of the acylated ICI intermediate QM4 (see Scheme 2) indicated the molecular ion M⁺ at m/z = 383, and the expulsion of the ethyl group. Also we noted the loss of CH₂=C=O from M⁺, leaving the ICI intermediate. Characteristic fragmentation of the latter shows in peaks at m/z = 118 and 169. The peak at m/z = 118 can be rationalized by formation of the [CH=CH-NH-Ph]⁺ ion via α -fission with respect to the oxazole ring, and that at m/z = 169 by framentation via the generalized RCN-type fission of oxazole heterocycles, as indicated in our previous work.⁸

NMR measurements

We start the interpretation of the NMR spectroscopic measurements of 1-11 with the ¹H NMR signals of 1. In the aromatic region (7.2< δ <8.6) four peaks are found: two doublets and two triplets. The two doublets are easily assigned to H(3) and H(6) [Fig. 1(a)]. H(6) is assigned to the signal at low field, *i.e.* at δ 8.55, $J(ortho)=J(H_6-H_5)=9$ Hz, because H(6) is in the ortho position to the N atom. Then H(3) is assigned to δ 8.07, $J(ortho)=J(H_3-H_4)=7$ Hz. The triplet at δ 7.68, J(ortho)=9 Hz, is assigned to H(5), and the other triplet with δ 6.90, J(ortho)=7 Hz, is assigned to H(4). The signals of the alkyl hydrogen atoms in the spectrum are easily recognized.

With reference to the ¹³C NMR spectra of 1, the peak at δ 184.0 is assigned to C2'=S, the one at δ 161.8 is assigned to C4'=O, and the peak at δ 80.21 to C5'. Other signals were assigned according to the previous NMR spectra of blue sensitizing dyes⁹ and reference NMR data.¹¹

¹H and ¹³C NMR assignments of 1 were then transferred to the other blue-sensitizing compounds included in Tables 5–8.

Chemical shift assignments for the green-sensitizing dyes are based on carbon-hydrogen 2D correlation spectra combined with assigned carboxazole spectra and standard substituent increments.¹¹ The results are collected in Tables 9 and 10. Shift values, coupling patterns and coupling constants unequivocally prove the structure of 9. Moreover, the vicinal coupling constant ${}^{3}J[H(8)-H(9)]=13.1$ Hz shows the *E* configuration of the C(8)-C(9) moiety [see Fig. 1(*e*) for numbering].

Turning to the averaged ¹³C NMR shifts in the merocyanines, one notes (Fig. 2) that the central atom in the zeromethine

C(4)

C(5)

C(6)

 CH_2

CH₃

C(2')

C(4')

C(5')

CH₂

CH₃

¹³C NMR^a ¹H NMR 1 2 3 1 2 atom atom pyridine moiety H(3)8.07 8.09 8.30 C(2) 137.50 137.46 H(4) 6.90 6.93 7.13 C(3) 123.33 123.81

7.68

8.72

4.39

1.41

7.89

8.60

4.27

4.81

Table 5 ¹H and ¹³C chemical shifts (δ , ref. Me₄Si) to zeromethine pyridine rhodanine dyes in deuteriated Me₂SO at 30 °C [atomic numbering is given in Fig. 1(*a*); atom H(i) is attached to C(i)]

^aThe solubility of 3 was too low for its ¹³C NMR spectrum to be measured. ^bThe chemical shift of the CH_2 group coincides with those of the solvent Me₂SO.

4.04

1.15

142.67

114.64

149.02

45.84

184.04

161.75

80.21

39.08^b

12.03

141.54

115.12

148.24

52.00

15.45

183.84

162.06

79.45

39.08^b

12.03

Table 6 ¹H and ¹³C chemical shifts (δ , ref Me₄Si) and ³J(H–H) coupling constants (in Hz) of 4 in deuteriated Me₂SO at 30 °C [atomic numbering is given in Fig 1(b), atom (H(1) is attached to C(1)]

	atom	δ	area	$J/{ m Hz}$	atom	δ
benzothiazole moiety				······································	C(2)	153 93
					C(3a)	139 59
	H(4)	791	1H, dd	$H_4-H_6, 1$ $H_4-H_5, 8$	C(4)	124 12
	H(5)	7 50	1H, dt	$H_5 - H_7, 1$ $H_5 H_6, 8$	C(5)	125 40
	H(6)	7 34	1H, dt	$H_{4} - H_{6}$, 1 $H_{6} - H_{7}$, 8	C(6)	127 29
	H(7)	7 76	1H, dd	$H_6 H_7, 8$	C(7)	112 38
					C(7a)	122 33
benzothiazole-alkyl side chain	H(8)	4 36	2H, t	H ₈ -H ₉ , 73	C(8)	44 89
	H(9)	1 88	2H, m	$H_8 - H_9, 73$ $H_9 - H_{10}, 73$	C(9)	27 77
	H(10)	1 78	2H, m	$H_9 H_{10}, 73$ $H_{10} H_{11}, 73$	C(10)	22 09
	H(11)	2 50	2H, t	$H_{10}-H_{11}$, 73	C(11)	50 46
	H(12)	8 94	1H		, , ,	
	H(13)	3 08	6H, q	$H_{13}-H_{14}$, 73	C(13)	45 77
	H(14)	1 17	9H, t	$H_{13} - H_{14}$, 73	C(14)	8 50
rhodanine mojety					C(2)	187 10
					C(4)	167 45
					C(5)	81 61
rhodanıne–alkyl sıde chaın	H(6)	4 71	2H		C(6)	46 90
-					C(7)	164 15

Table 7 ¹H and ¹³C chemical shifts (δ , ref Me₄Si) of zeromethine benzothiazole rhodanine dyes 5 7 in deuteriated Me₂SO at 30 °C [atomic numbering is given in Fig 1(c), atom H(1) is attached to C(1)]

	¹ H NMR				¹³ C NMR ^a		
	atom	5	6	7	atom	5	7
benzothiazole moiety	H(4)	7 93	7 93	7 91	C(2)	153 51	154 76
	H(5)	7 52	7 51	7 50	C(3a)	139 26	140 16
	H(6)	7 35	7 35	7 33	C(4)	124 09	124 00
	H(7)	7 68	7 66	7 65	C(5)	125 67	125 30
					C(6)	127 31	127 15
					C(7)	111 85	112 07
					C(7a)	122 50	122 34
benzothiazole-alkyl side chain	CH ₂	4 41			CH ₂	42 23	
-	CH ₃	1 42	3 99	3 96	CH ₃	14 06	40 12 ^b
rhodanine moiety					C(2)	186 72	187 32
2					C(4)	164 58	164 04
					C(5)	82 04	82 57
rhodanine–alkyl side chain	CH ₂	4 10	4 10	4 70	CH,	39 96 ^b	40 12 ^b
,	CH ₃	1 20	1 18		CH ₃	11 95	

^aThe solubility of 6 was too low for its ¹³C NMR spectrum to be measured ^bThe chemical shift of the CH_2 group coincides with those of the solvent Me_2SO

Table 8 ¹H and ¹³C chemical shifts (δ , ref Me₄S1) of zeromethine benzimidazole rhodanine dye 8 in deuteriated Me₂SO at 30 °C [atomic numbering is given in Fig 1(d), atom H(1) is attached to C(1)]

	¹ H NMR		¹³ C NMR	
benzimidazole moiety	H(4),H(7) H(5),H(6)	7 72 7 44	C(2) C(3a),C(7a) C(4),C(7) C(5),C(6)	150 22 147 46 110 95 124 32
benzımıdazole-alkyl sıde chain	CH ₃	3 81	CH ₃	39 90ª
rhodanine moiety			C(2) C(4) C(5)	184 49 160 39 80 15
rhodanıne-alkyl sıde chaın	CH ₂ CH ₃	4 04 1 18	CH ₂ CH ₃	32 99 11 94

"The chemical shift of the CH₃ group coincides with those of the solvent Me₂SO

Table 9 ¹H and ¹³C chemical shifts (δ , ref. Me₄Si) and ³J(H–H) coupling constants (in Hz) of **9** in deuteriated Me₂SO at 30 °C [atomic numbering is given in Fig. 1(*e*); atom H(i) is attached to C(i)]

¹ H NMR				¹³ C NMR		
atom	δ	area	J/Hz	atom	δ	
				C(2)	160.56	
				C(3a)	132.08	
H(4)	7.76	1H, d	$H_4 - H_6$, 1.8	C(4)	107.93	
. ,				C(5)	137.84	
H(6)	7.51	1H, dd	$H_4 - H_6$, 1.8	C(6)	122.10	
· · /		,	$H_{6}-H_{7}$, 8.5			
H(7)	7.63	1H, d	$H_{6}-H_{7}$, 8.5	C(7)	110.21	
· /			0	C(7a)	145.76	
H(8)	5.31	1H, d	$H_8 - H_9$, 13.1	C(8)	76.82	
H(9)	7.82	1H, d	$H_8 - H_9$, 13.1	C(9)	132.15	
. /			0	C(10)	139.24	
H(11)	7.72	2H, dd	$H_{11}-H_{13}$, 1.4	C(11)	126.90	
. ,			$H_{11} - H_{12}$, 7.9	. ,		
H(12)	7.48	2H, t	$H_{11}-H_{12}$, 7.9	C(12)	128.77	
H(13)	7.40	1H, tt	$H_{11} - H_{13}$, 1.4	C(13)	127.53	
• •		-	$H_{12}-H_{13}$, 7.5			
H(14)	4.01	2H, q	$H_{14} - H_{15}$, 7.17	C(14)	38.76	
H(15)	1.31	3H, t	$H_{14}-H_{15}$, 7.17	C(15)	12.28	
· · /			14 137	$\mathbf{C}(2')$	189.65	
				C(4')	165.04	
				C(5')	104.01	
H(6')	4.19	2H	$H_{60} - H_{70}$, 7.02	C(6')	38.88	
H(7′)	1.14	3H	H _{6'} ,-H _{7'} , 7.02	C(7')	11.95	

Table 10 ¹H and ¹³C chemical shifts (δ , ref. Me₄Si) of dimethine benzoxazole rhodanine dyes **10** and **11** in deuteriated Me₂SO at 30 °C [atomic numbering is given in Fig. 1(*f*); atom H(i) is attached to C(i)]

	¹ H NMR			¹³ C NMR	
	10	11		10	11
			C(2)	161.18	160.82
			C(3a)	132.59	133.28
H(4)	7.19	7.69	C(4)	96.35	110.03
			C(5)	157.39	129.26
H(6)	6.76	7.22	C(6)	110.25	122.77
H(7)	7.46	7.55	C(7)	109.09	110.98
			C(7a)	140.16	144.90
H(8)	5.35	5.36	C(8)	77.17	77.00
H(9)	7.78	7.75	C(9)	132.25	131.84
H(10)	4.07	4.06	C(10)	42.76	45.57
H(11)	1.72	1.78	C(11)	25.86	25.78
H(12)	1.72	1.73	C(12)	22.06	21.98
H(13)	2.51	2.55	C(13)	50.44	50.45
OCH ₃	3.80		OCH ₃	56.04	56.04
			C(2')	189.54	190.03
			C(4')	164.97	165.13
			C(5')	103.38	105.25
H(6')	4.00	4.00	C(6')	42.76	42.91
H(7′)	1.13	1.15	C(7')	11.96	11.96

zeromethine rhodanines



Fig. 2 Comparison of ¹³C chemical shifts (ppm) in merocyanine dyes

chain of compounds 1-8 has a lower shift value (upfield shift) and in the dimethine chain of compounds 9-11 it has a higher shift value (downfield shift). It follows that the π -electron density in the dimethine chain is lower than that in the zeromethine chain.^{9,12} This conclusion is in accordance with a simple count of the number of π -electrons per C atom present in each methine cyanine system. Moreover, the vinylogous elongation of the cyanine system and the accompanying changes in the electron distribution can be rationalized with the electron-in-a-box description.¹³⁻¹⁵ In a zeromethine chain the number of π -electrons is 6, and hence in the highest occupied molecular orbital (HOMO) there is a maximum π electron density at the position of the central C atom. In contrast, in the dimethine chain the number of π -electrons is 8, and thus in the HOMO there is a minimum π -electron density at the position of the central C atom. In accordance with this view one observes in the dimethine series significantly higher shift values (downfield shifts) in the central and adjoining C, H.

The differences induced in the pyridine ring when N-CH₃ is replaced by N-C₂H₅ may be studied by comparison of 1 and 2 [Fig. 1(*a*)]. It is seen that in 2, with the exception of H(5), all H atoms have higher δ values (downfield shifts), whereas C(2) and C(6), which are directly attached to N, have lower δ values (upfield shifts). This behaviour suggests a more positive charge on the N-ethyl substituent and is in accordance with our earlier research on other blue-sensitizing, pyridine-containing monomethine cyanine sensitisers.⁹

UV-VIS and reflection spectra

The absorption maxima and molar extinction coefficients for the dye monomers 1–11 are shown in Table 11. It can be seen that change of the N-substituents has little effect on the spectra of the dyes. Significant hypsochromic shifts are seen when pyridine is replaced by benzothiazole. Further hypsochromic shifts are seen when benzothiazole is in turn replaced by benzimidazole. This is due to the decrease of the π -electron density in the heterocyclic rings. In the series 9–11, bathochromic shifts are seen, caused by substituents on the 5-position of the heterocyclic ring, following the sequence OCH₃>Ph>Cl.

Dyes 6 and 7 were added to coated $Ag^{l}Br$ T-grain emulsions, and the reflection spectra were recorded. Both spectra showed J-aggregation behaviour. Dye 6 showed a molecular peak at 430 nm and a J-aggregation peak at 450 nm (Fig. 3), and 7 showed a molecular peak at 435 nm and a J-aggregation peak at 465 nm (Fig. 4).

MOPAC calculations and electrochemical measurements

Based on the optimised geometries obtained from the MOPAC calculations, the ionization potentials (I_s^{th}) and electron affinities (E_{aff}) of dyes 1-3, 5 and 7 were calculated (see Table 12), which may be related to the energy levels of the HOMO and

Table 11 UV-VIS data for 1-11 in the monomeric state (dye concentration ca. 5×10^{-6} mol l^{-1} in methanol)

dye	$\lambda_{ m max}/ m nm$	$\varepsilon/10^4 \mathrm{l}\mathrm{mol}^{-1}\mathrm{cm}^{-1}$
1	455	6.4
2	455	1.3
3	453	4.1
4	426	1.8
5	428	4.1
6	427	0.6
7	425	0.7
8	408	1.4
9	496	5.0
10	500	3.4
11	491	3.0



Fig. 3 Reflectance spectrum of 6



Fig. 4 Reflectance spectrum of 7

Table 12 Oxidation potentials (E_{ox}) , ionization potentials (I_s^{th}) , reduction potentials $(E_{\rm rd})$ and electron affinities $(E_{\rm aff})$ of the zeromethine merocyanine compounds

dye	E_{ox} /V vs. SCE	$I_s^{\rm th}/{\rm eV}$	$E_{\rm rd}/{\rm V}$ vs. SCE	$E_{\rm aff}/{ m eV}$
1	0.583	8.12	-1.622	1.379
2	0.609	8.11	-1.640	1.391
3	0.668	8.22	-1.584	1.551
5	0.862	8.47	-1.641	1.573
7	0.900	8.53	-1.736	1.696

LUMO, respectively. In fact, the difference $I_s^{\text{th}} - E_{\text{aff}}$ in 1-3 amounts to ca. 6.7 eV, compared to ca. 6.9 eV in 5 and 7. This agrees with the larger λ_{max} values (ca. 455 nm) observed in the UV-VIS spectra of 1-3, compared to the smaller λ_{max} values (ca. 428 nm) measured for 5 and 7.

Charge distributions, calculated for 2, 5 and 8 are given in Fig. 5. A comparison with NMR data (Fig. 2, and Tables 5-8) shows the following. First, the charges on the central C atoms [*i.e.* C(5')] of the merocyanine systems (N-C=C-C=O) are highly negative and indicate maximum π -electron density. This result is in line with the NMR measurements and the electronin-a-box theory. Furthermore, the ${}^{13}C$ chemical shifts of C(5') increase in the same order as the charge densities decrease when going from 2 (pyridine dye) to 8 (benzimidazole dye) to 5 (benzothiazole dye). Secondly, the charge on the N atom of the rhodanine heterocycle is always smaller than that on the N atom of the other heterocycle, a result also reflected in the available NMR data. In fact, in the ¹³C NMR spectra of 2 and 5 the ethyl group attached to the N position of the pyridine and benzothiazole moieties, respectively, shows higher δ values (downfield shifts) than the ethyl group attached to the





(a)

Fig. 5 Charge distribution of the merocyanine dyes: (a) 2, (b) 5, (c) 8

N position of the rhodanine heterocycle. We have earlier interpreted this observation to reflect the lower positive charge on the rhodanine N atom.

Table 12 also lists the measured oxidation potentials (E_{ox}) of dyes 1-3, 5 and 7. When we assume that the bandgap is equal to the optical excitation energy E_{tr} of the merocyanine (the longest wavelength of the UV absorption), and ignore solvatation energies, the reduction potential (E_{rd}) can be



Fig. 6 Relation between the oxidation potential $(E_{ox}/V \text{ vs. SCE})$ and ionization potential (I^{th}_{s}/eV)



Fig. 7 Relation between the reduction potential ($E_{\rm rd}/V$ vs. SCE) and ionization potential ($E_{\rm aff}/eV$)

Table 13 Sensitometric properties of the blue-sensitizing dyes 1–5, 7 and $8^{\rm a}$

dye	A ^b /ml	D_0^c	S^d (DIN)	γ ^e	D_{\max}	solubility
control	0	0.05	20	21	4.05	
1	2	0.05	20	2.4	4.05	rood
1	23	0.00	21	2.0	3 37	goou
2	2	0.06	21	2.2	4.63	rood
-	3	0.06	22	2.0	4.05	good
control	õ	0.08	21.5	2.4	6.03	
3	0.5	0.00	21.0	2.4	5.89	poor
0	1	0.24	17.5	20	5.90	poor
	2	0.24	18.0	2.0	5 74	
control	õ	0.09	21	3.0	5.67	
4	2	0.02	20	24	5 74	good
-	ĩ	0.41	18	2.4	5 44	good
	4	0.41	15	2.5	5 41	
control	ó	0.08	21.5	2.5	5 28	
5	õ 5	0.08	20.0	20	4 34	noor
-	1	0.08	20.0	2.0	5.49	poor
	2	0.07	18.5	2.0	4.40	
control	ō	0.09	21	3.0	5.54	
7	2	0.14	20	2.8	5 54	noor
•	3	0.20	20	2.8	5 71	peer
	4	0.23	19	2.6	5.44	
control	Ó	0.05	20	2.4	4.05	
8	2	0.08	20	2.0	5.90	good
-	3	0.09	20	2.2	4.55	5000

^aThe solubility in H₂O of **6** is too low to measure its sensitizing properties. ^bA = number of ml added of a 0.2% solution of dye in MeOH to 50 g emulsion. ^cD₀, D_{max} = minimum and maximum optical density of photographic plate. ^dS = sensitivity of photographic plate in DIN (Deutsche Industrie Norm; see ref. 17). ^e\gamma = contrast.

evaluated6 by

$$E_{\rm rd} = E_{\rm ox} - E_{\rm tr} \tag{1}$$

Calculated one-electron reduction values are also reported in Table 12.

A least-squares fit of the oxidation potentials (E_{ox}) found electrochemically vs. the MOPAC calculated ionization potentials (I_s^{th}) gave a linear relation with correlation coefficient $\gamma =$ 1.00, as depicted in Fig. 6:

$$I_{\rm s}^{\rm th} = 1.355 E_{\rm ox} + 7.308 \tag{2}$$

The correlation between the reduction potential $(E_{\rm rd})$ and the electron affinity $(E_{\rm aff})$ was also enumerated, giving a straight line with $\gamma = 0.98$, as depicted in Fig. 7:

$$E_{\rm aff} = 0.997 E_{\rm rd} + 3.050 \tag{3}$$

Table 14 Sensitometric properties of the green-sensitizing dyes 9-11ª

dye	A/ml	Do	S (DIN)	γ	D_{\max}	solubility
control	0	0.08	21.5	2.4	5.28	
9	0.5	0.07	21.5	2.4	5.08	poor
	1	0.10	21.5	2.4	5.11	-
	2	0.10	23.0	2.4	4.85	
10	0.5	0.07	21.5	2.3	4.53	poor
	1	0.08	20.0	2.2	5.68	•
	2	0.07	21.5	2.2	5.36	
control	0	0.08	21.5	2.4	5.82	
11	0.5	0.17	20.0	2.5	4.05	good
	1	0.20	19.0	2.5	4.89	e
	2	0.32	15.5	2.2	4.70	

"For definitions, see footnotes to Table 13.

Furthermore, the oxidation potential of 2, which showed sensitizing properties, was reversible, whereas those of the desensitizers (3, 5, 7) were irreversible which suggests that when the desensitizers lose an electron, the remainder of the compound is not stable.

Performance in photographic emulsions

The results of the experiments with photographic emulsions for dyes 1-8 are given in Table 13, and those for dyes 9-11are reported in Table 14. It follows that 2 and 9 show sensitizing properties in emulsions, while most other dyes are desensitizers. These results coincide with former work on rhodanine merocyanine dyes,⁴ except for 7, which does not show any sensitizing properties in our work.

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