Long Chain Heterocyclic Dyes. Part One. Hydrophobic Structures [1]

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A series of polymethine dyes and of their precursors, containing long and short alkyl chains, was prepared and their chemical and spectroscopic (uv, ^{1}H-nmr) properties were briefly discussed. The electronic absorption spectra of the dyes in aqueous medium and in presence of anionic or cationic surfactants evidenced aggregation phenomena. The best deaggregating effect was shown by the anionic surfactant when added above its critical micellar concentration.

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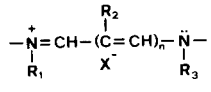
Our recent studies on the preparation of heteroaromatic bases, of their quaternary salts and of the related polymethine dyes [2-5] have led us to investigate the nature of new dyes containing long chains and one or two positive charges. These structures were studied for their surface activity [6-8].

This paper deals with a series of polymethine dyes characterized by a classical 'amidinium ion' depicted under the general formula I in which the nitrogen atoms may or



may not be part of a heterocycle (pyridine, quinoline, benzoxazole, benzothiazole, benzimidazole), where n is 2, 3 or 4, X^- is iodide, chloride, bromide or perchlorate, R_2 is hydrogen, methyl or ethyl , and R_1 and R_3 are methyl, carboxymethyl, *n*-dodecyl, *n*-hexadecyl. The individual structures are summarized in Tables 1-3. The Scheme below, uses the benzothiazolium salt as an example to demonstrate the pathways to the families of long chain dyes. Some properties of the dyes were investigated with particular emphasis on those dyes possessing hydrophobic alkyl chains; the intermediate quaternary salts have also been considered.

To obtain the dyes, the heteroaromatic bases were quaternarized with suitable agents in order to enhance the reactivity of the methyl groups conjugated to the quaternized site. For long chain derivatives, the reaction was better controlled by an excess of base in respect to the quaternizing agent: in fact, dehydrohalogenation of alkyl halides sometimes occurred and the hydrohalogenides of the bases were formed. The use of an excess of base gave the best results, limiting this undesired side reaction. The X^- anions were changed in the single cases in order to modify the solubility of the dyes in water. From the quaternization of 2-methylbenzimidazole, a step which, as previously observed [7], could give different products, only the bis-*N*-alkylated salt **10** was recovered. The R_f values of the salts are consistent with the polarity of their structures. Salts **5** and **8** are highly retained on the polar substrate owing to the presence of short chains and of polar groups, while the other salts show a distinct higher mobility.

The dyes were obtained from the corresponding salts by the usual methods. For the synthesis of the 'meso' ethylthiacarbocyanine **23**, it was necessary to prepare the ketone **30**. It is interesting to compare the absorption spectrum of this compound with the spectrum of the parent quaternary salt **7** (Figure 1). In the latter, the main absorption is characteristic of heteroaromatics, while in

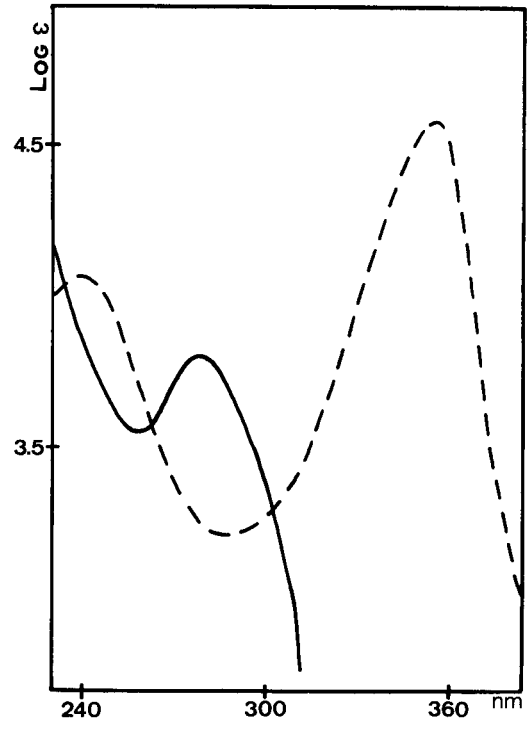
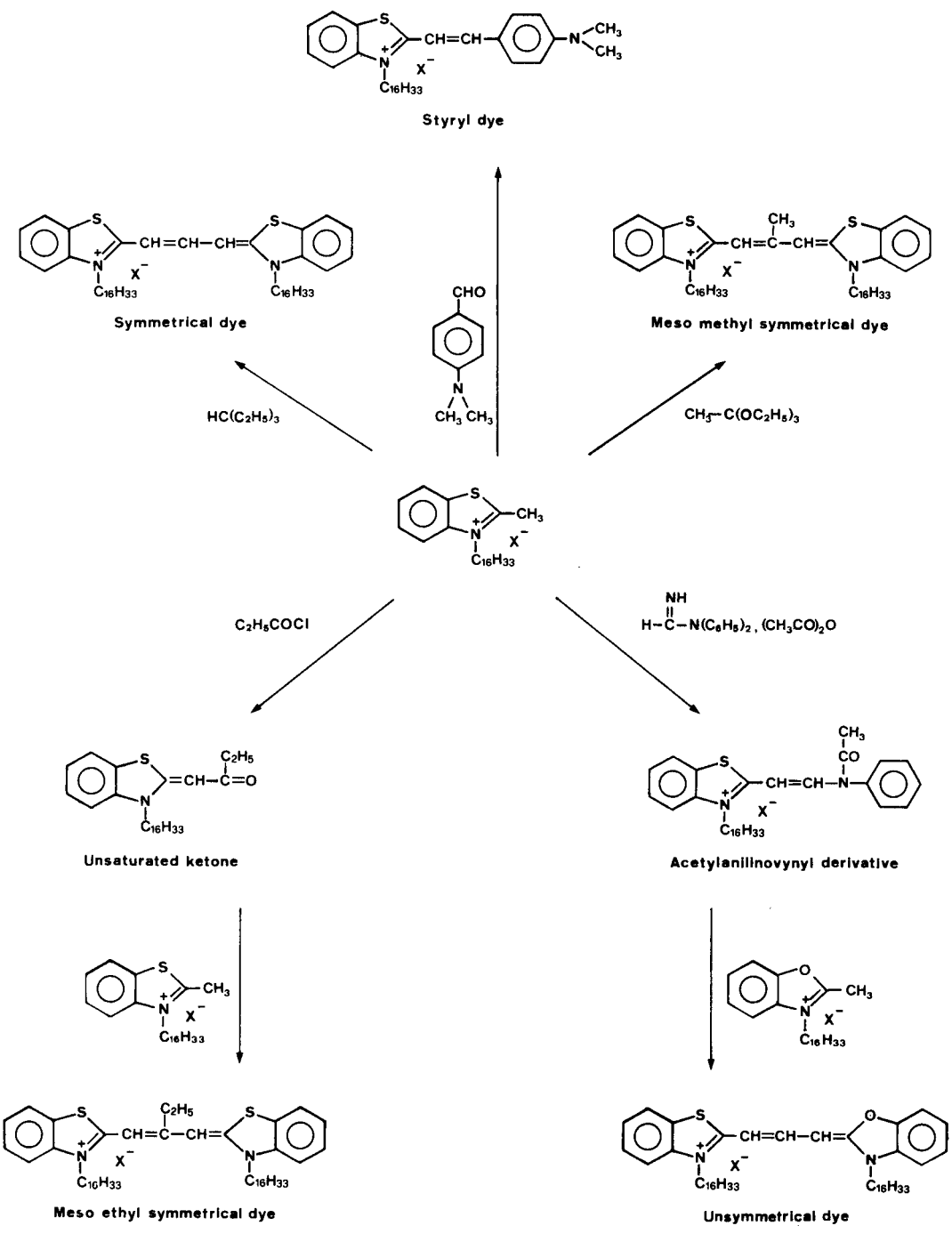
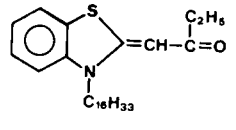


Figure 1. Electronic absorption spectra in ethanol of compounds: n. **7** —; n. **30** ---.





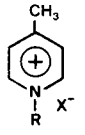
30

the first the chromogen responsible for the long wavelength band is a substituted α,β-unsaturated carbonyl. The R_f values of the dyes are systematically higher than those of the parent quaternary salts.

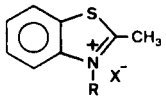
The long chain salts have, as expected, electronic absorption spectra in alcohol solution very similar to their *N*-methyl counterparts. The variation in the patterns, the positions and the intensities of the absorption maxima are within experimental errors. The *N*-carboxymethyl salts show a similar behaviour insofar as the long wavelength band is concerned, while, at shorter wavelengths, a second absorption appears as illustrated by the example in Figure 2.

Table 1

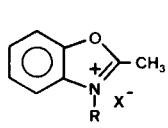
Characterisation Data of Quaternary Salts



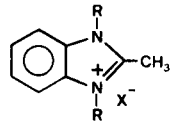
n. **1-5**



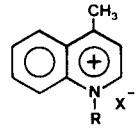
n. **6-8**



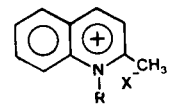
n. **9**



n. **10**



n. **11**



n. **12**

Compound number	Structure R =	X =	Yield %	Mp °C	R_f	Crystallization solvent [a]	Empirical formula	Elemental Analyses Calcd./Found C	H	N	Electronic absorption spectra λ max nm (log ε) [b]	NMR (δ) ≡CCH_3	≡^+N-CH_2···
1	$C_{12}H_{25}$	I^-	64	73-74	0.30	A	$C_{18}H_{32}IN$	55.52 55.48	8.28 8.33	3.60 3.56			
2	$C_{12}H_{25}$	Cl^-	78	51-52	0.38	A	$C_{18}H_{32}ClN$	72.56 72.50	10.83 10.87	4.70 4.81	256 (3.61)	2.62	4.62
3 [c]	$C_{16}H_{33}$	I^-	75	82-84	0.30	B	$C_{22}H_{40}IN$	59.32 59.25	9.05 8.97	3.14 3.06			
4 [c]	$C_{16}H_{33}$	Cl^-	85	75-76	0.37	B	$C_{22}H_{40}ClN$	74.64 74.52	11.39 11.45	3.96 3.92			
5	CH_2COOH	Cl^-	94	180 dec	0.08	C	$C_8H_{10}ClNO_2$	51.21 51.18	5.37 5.26	7.46 7.35	256 (3.81)	2.50	5.10
6	$C_{12}H_{25}$	I^-	65	126-127	0.35	C	$C_{20}H_{32}INS$	53.93 53.85	7.24 7.30	3.14 3.11	277 (3.80)	3.25	4.77
7 [d]	$C_{16}H_{33}$	I^-	53	127-129	0.33	C	$C_{24}H_{40}INS$	57.47 57.38	8.04 8.11	2.79 2.71	277 (3.80)	3.30	4.77
8	CH_2COOH	Cl^-	51	190 dec	0.11	C	$C_{10}H_{10}ClNO_2S$	49.28 49.19	4.14 4.20	5.75 5.69	278 (3.82)	3.12	5.66
9	$C_{16}H_{33}$	I^-	10	88-90	0.31	D	$C_{24}H_{40}INO$	59.37 59.32	8.30 8.35	2.89 2.83	276 (3.61)	3.33	4.67
10	$C_{16}H_{33}$	Br^-	32	238-239	0.55	C	$C_{40}H_{73}BrN_2$	72.58 72.48	11.12 11.19	4.23 4.17	278 (3.91) 270 (3.88) 255 (3.75)	3.30	4.63
11	$C_{16}H_{33}$	Br^-	81	68-70	0.36	C	$C_{26}H_{42}BrN$	69.62 69.57	9.44 9.48	3.12 3.06	314 (3.89) 235 (4.62)	3.16	5.48
12	$C_{16}H_{33}$	Br^-	9	217-219	0.31	C	$C_{26}H_{42}BrN$	69.62 69.55	9.44 9.53	3.12 3.09	315 (3.97) 309 (3.80) 303 (3.84)	3.18	5.00

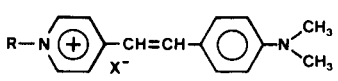
[a] A = glacial acetic acid; B = ethanol/water; C = ethanol; D = 2-propanol. [b] The λ max and log ε values correspond to the most intense peak of the long-wavelength band. [c] See also ref [14]. [d] See also ref [6].

The spectra of the long chain dyes in alcohol solution obey the Beer-Lambert law; the spectral patterns closely resemble those of short chain dyes. The positions of the maxima are however 2-6 nm shifted towards longer wavelengths probably a result of solvation effects. Also in the case of dyes, the *N*-carboxymethyl derivatives have a different behaviour and this results in a distinct hypsochromic shift of the main broad band.

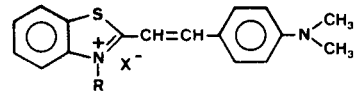
In the nmr spectra of the salts, only the signals of the 2 and 4 methyl groups and of the first methylenic group, directly linked to the quaternarized nitrogens, are easily detectable as broadened singlets and triplets, respectively. The aromatic protons and the remaining protons of the long chains appear as complex, unresolved signals whose integration is consistent with the assigned structures. The positions of the signals of methyl and aromatic protons are

Table 2

Characterisation Data of Styryl Dyes



n. **13-18**



n. **19-20**

Compound number	Structure R =	X =	Yield %	Mp °C	R_f	Crystallization solvent [a]	Empirical formula	Elemental Analyses Calcd./Found C	H	N	Electronic absorption spectra λ max nm (log ε)	NMR (δ) ≡$^{+}$N-CH$_2$···
13 [b]	$C_{12}H_{25}$	Cl^-	46	231-233	0.73	B	$C_{27}H_{41}ClN_2$	75.57	9.63	6.53	482	4.42
								75.45	9.51	6.43	(4.60)	
14	$C_{12}H_{25}$	ClO_4^-	58	184-185	0.70	C	$C_{27}H_{41}ClN_2O_4$	65.77	8.38	5.68	482	4.42
								65.57	8.23	5.37	(4.65)	
15	$C_{16}H_{33}$	I^-	86	241-242	0.73	C	$C_{31}H_{49}IN_2$	64.57	8.57	4.86	482	4.42
								64.71	8.41	4.93	(4.65)	
16	$C_{16}H_{33}$	NO_3^-	60	206-207	0.76	C	$C_{31}H_{49}N_3O_3$	72.76	9.65	8.21	482	4.42
								72.59	9.74	8.17	(4.64)	
17	$C_{16}H_{33}$	Cl^-	38	245-247	0.65	C	$C_{31}H_{49}ClN_2$	76.74	10.18	5.77	482	4.42
								76.81	10.18	5.86	(4.62)	
18	CH_2COO^-	—	51	191-193	0.34	C	$C_{17}H_{18}N_2O_2$	72.32	6.43	9.92	472	4.02
								72.21	6.51	9.75	(4.61)	
19	$C_{12}H_{25}$	I^-	48	188-189	0.76	C	$C_{29}H_{41}IN_2S$	60.41	7.17	4.86	530	4.75
								60.43	7.26	4.71	(4.84)	
20	CH_2COO^-	—	66	157-158	0.42	E	$C_{19}H_{18}N_2O_2S$	67.43	5.36	8.28	521	4.68
								67.36	5.41	8.26	(4.72)	

[a] B = ethanol/water, C = ethanol, E = water. [b] See also ref [6].

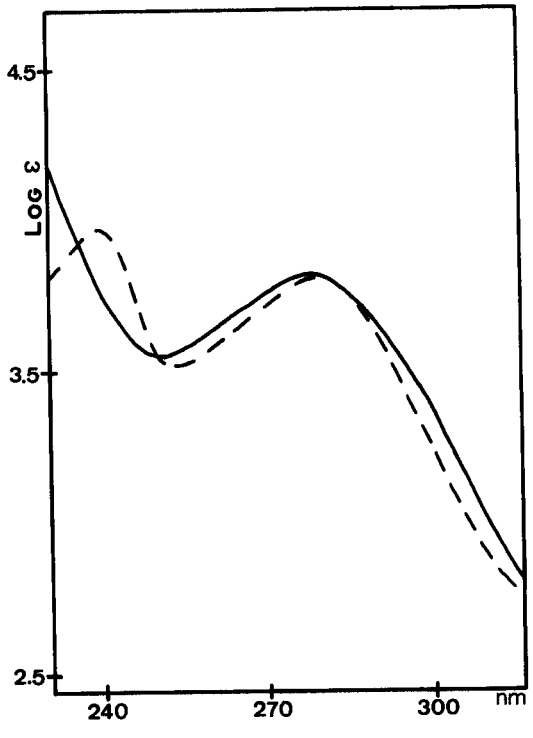


Figure 2. Electronic absorption spectra in ethanol of compounds: n. **6** —; n. **8** ---.

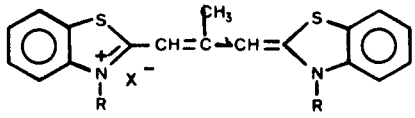
nearly the same as in the short chain salts. The signals of the methylene protons of the *N*-carboxymethyl groups are shifted downfield in comparison to their counterparts in the long chains owing to the deshielding effect of the carboxyl group. The above protons result deshielded by the charged heteroaromatic rings according to the sequence: lepidinium > quinaldinium > benzothiazolium > benzoxazolium > benzimidazolium > pyridinium.

In the nmr spectra of dyes, the signals of methyl protons, unless belonging to a 'meso' structure, are absent, while signals due to the polymethinic chains appear. Aromatic and long chain protons exhibit complex signals with proper integrations as in the salts. The first methylene protons show resonances upfield from the corresponding signals in the parent salts owing to the enhanced delocalization of the positive charge throughout the whole chromogen. The coupling constants of the methine protons of polymethine chains (not detectable for 'meso' structures due to the absence of vicinal protons) are in the range 12-16 Hz and this supports the presence of trans forms in DMSO solutions.

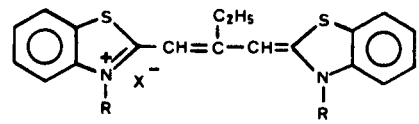
Studies on the aggregation of short chain dyes are well known [9,10]. In alcohol solutions no aggregations were evidenced, while in aqueous solutions the dimeric constants of association have been evaluated and more com-

Table 3

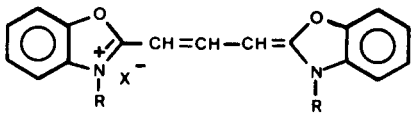
Characterisation Data of Symmetrical and Unsymmetrical Dyes



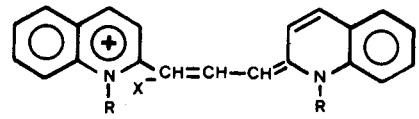
n. **21-22**



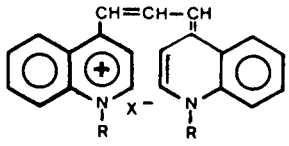
n. **23**



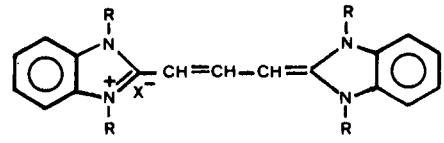
n. **24**



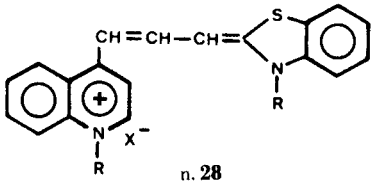
n. **25**



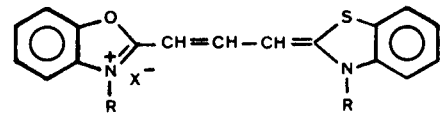
n. **26**



n. **27**



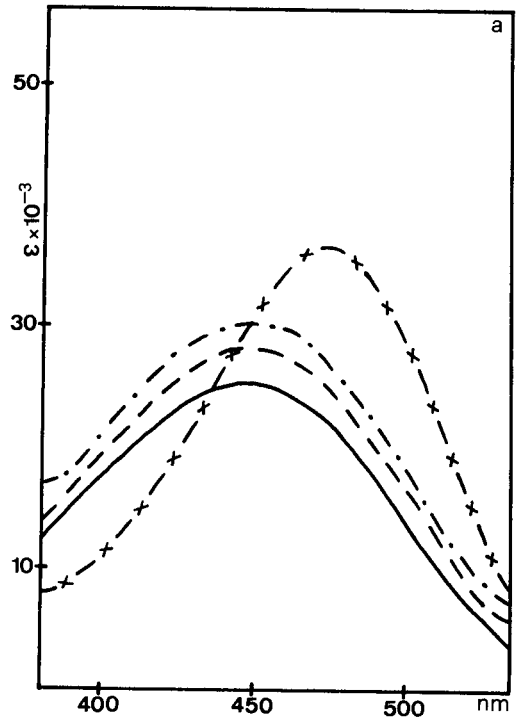
n. **28**

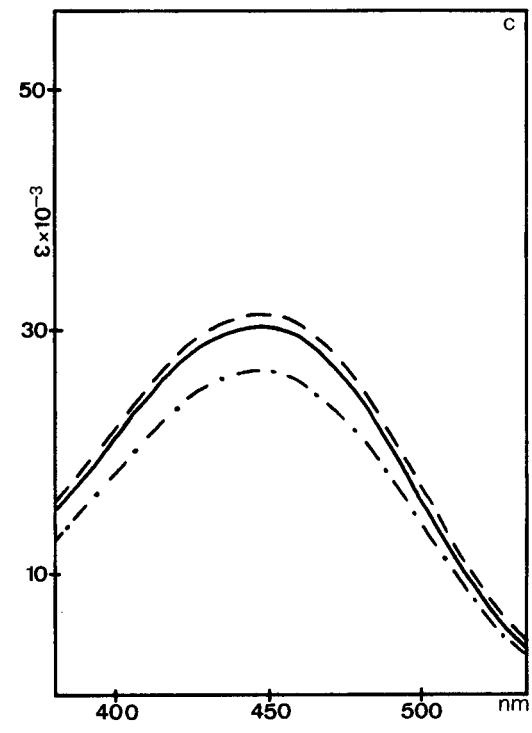


n. **29**

Compound number	Structure R =	X =	Yield %	Mp °C	R_f	Crystallization solvent [a]	Empirical formula	Elemental Analyses Calcd./Found C	H	N	Electronic absorption spectra λ max nm (log ε)	NMR (δ) ≡$^{+}$N-CH$_2$···
21	$C_{12}H_{25}$	I^-	61	165-167	0.90	C	$C_{42}H_{63}IN_2S_2$	64.10	8.07	3.56		
								64.23	7.96	3.60		
											547	4.52
22	$C_{12}H_{25}$	ClO_4^-	79	132-133	0.88	C	$C_{42}H_{63}ClN_2O_4S_2$	66.41	8.36	3.69		
											(5.07)	
								66.23	8.41	3.46	(5.07)	
23	$C_{16}H_{33}$	ClO_4^-	30	111-112	0.92	F	$C_{51}H_{81}ClN_2O_4S_2$	69.15	9.22	3.16	551	4.40 [e]
								69.23	9.17	3.25	(4.96)	
24	$C_{16}H_{33}$	I^-	25	181-183	0.78	G	$C_{49}H_{77}IN_2O_2$	68.99	9.10	3.28	487	4.25
								68.71	9.24	3.15	(5.15)	
25	$C_{16}H_{33}$	Br^-	24	171-172	0.85 [b]	C	$C_{53}H_{81}BrN_2$	77.05	9.82	3.39	607	4.27 [e]
								77.19	10.00	3.27	(5.06)	
26	$C_{16}H_{33}$	Br^-	41	103-104	0.36 [c]	D	$C_{53}H_{81}BrN_2$	77.05	9.82	3.39	711	4.40 [e]
								76.88	9.69	3.21	(5.35)	
27	$C_{16}H_{33}$	Br^-	26	126-128	0.37 [d]	C	$C_{81}H_{143}BrN_4$	77.65	11.50	4.47	504	4.43 [e]
								77.71	11.39	4.56	(5.11)	
28	$C_{16}H_{33}$	ClO_4^-	80	124-125	0.86	C	$C_{51}H_{79}ClN_2O_4S$	71.92	9.35	3.29	633	4.15 [e,f]
								71.75	9.33	3.18	(5.14)	
29	$C_{16}H_{33}$	ClO_4^-	40	137-139	0.81	G	$C_{49}H_{77}ClN_2O_5S$	69.92	9.22	3.33	524	4.30 [f]
								70.08	9.11	3.45	(5.14)	

[a] C = ethanol, D = 2-propanol, F = methanol, G = ethanol/2-propanol. [b] Cellulose F 254 Merck, eluent, chloroform:absolute ethanol 15:4. [c] Kieselgel 60 F 254 Merck, eluent, chloroform:absolute ethanol 15:4. [d] The elution was carried out in the dark in the conditions indicated in c. [e] Solvent deuteriochloroform. [f] Unresolved signals of two methylene groups.





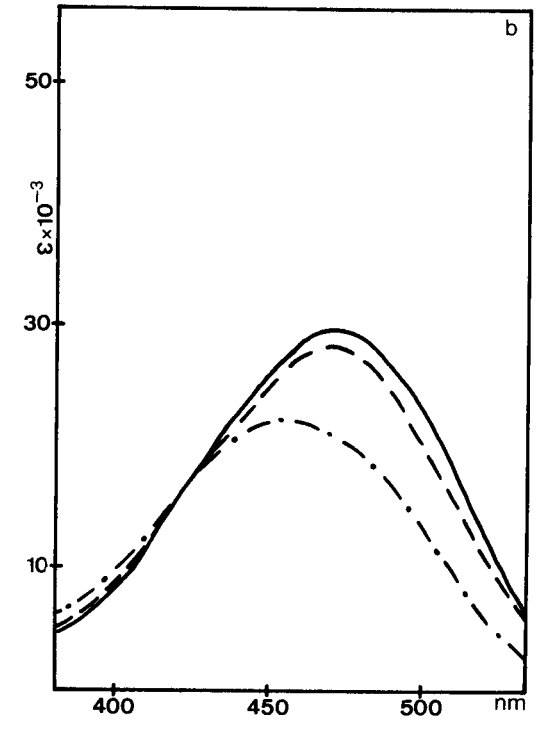
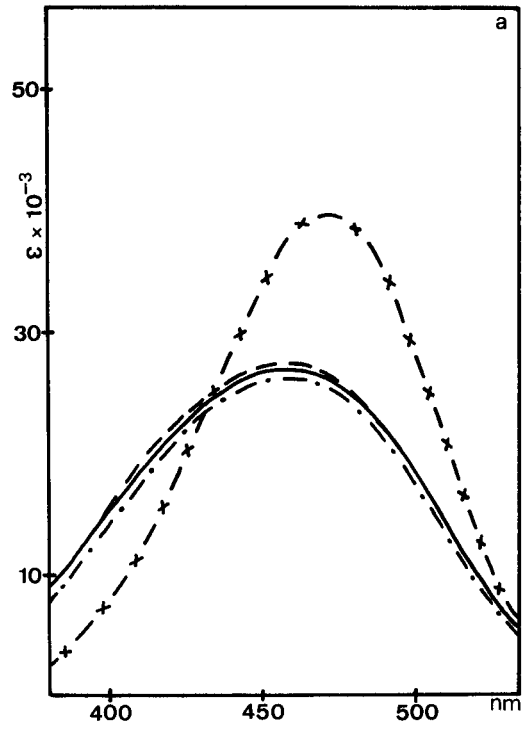


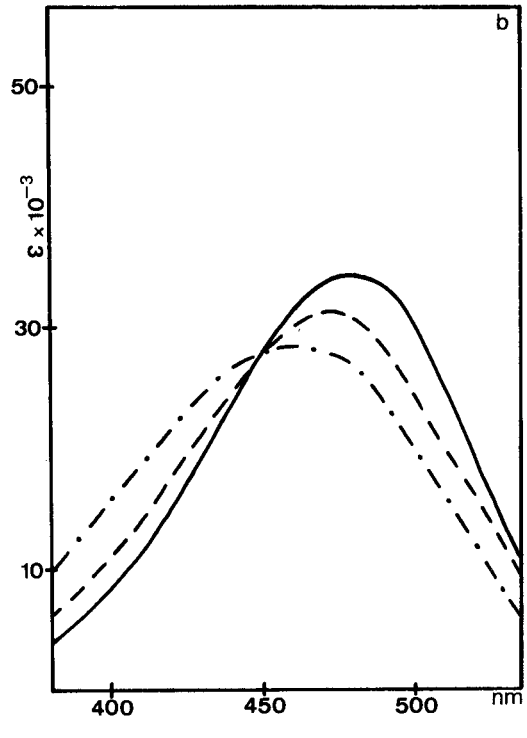
Figure 3. Spectra of dye n. **31**.
a -x-x- in methanol ($1 \times 10^{-5}M$); -•-•- in water ($0.5 \times 10^{-5}M$); --- in water ($1 \times 10^{-5}M$); — in water ($2 \times 10^{-5}M$).
b fixed cyanine ($2 \times 10^{-5}M$); variable SDS: — ($80 \times 10^{-3}M$); --- ($8 \times 10^{-3}M$); -•-•- ($4 \times 10^{-3}M$).
c fixed cyanine ($2 \times 10^{-5}M$); variable HTAB: — ($7 \times 10^{-3}M$); --- ($7 \times 10^{-4}M$); -•-•- ($7 \times 10^{-6}M$).

plex aggregates, named 'H' and 'J' aggregates, have been identified.

The investigations on compounds bearing long alkyl chains are not exhaustive and mainly concern the synthesis of dyes [11] and the formation of monolayers [12]. In a recent paper we studied the interaction of some cyanine dyes with synthetic vesicles and with an anionic surfactant [13].

We have now selected, among the seventeen dyes described herein, six structures representative of the main features: *e.g.* family of dyes, heterocyclic ring, chain length and a systematic survey on their spectral behaviour in different media are reported. For each dye, spectra are reported in methanol, in water at three concentrations (containing 5% methanol to enhance the solubility), and in aqueous solutions of sodium dodecylsulphate (SDS) and hexadecyltrimethylammonium bromide (HTAB) at different concentrations.





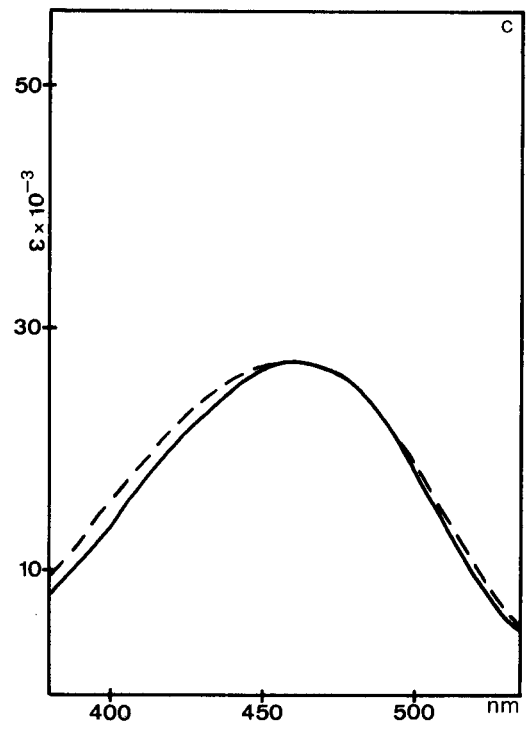
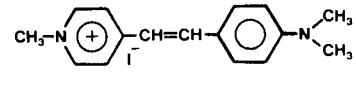


Figure 4. Spectra of dye n. **18**.
a -x-x- in methanol ($1 \times 10^{-5}M$); -•-•- in water ($0.5 \times 10^{-5}M$); --- in water ($1 \times 10^{-5}M$); — in water ($2 \times 10^{-5}M$).
b fixed cyanine ($2 \times 10^{-5}M$); variable SDS: — ($80 \times 10^{-3}M$); --- ($8 \times 10^{-3}M$); -•-•- ($4 \times 10^{-3}M$).
c fixed cyanine ($2 \times 10^{-5}M$); variable HTAB: — ($7 \times 10^{-3}M$); --- ($7 \times 10^{-4}M$ and $7 \times 10^{-6}M$ superimposed).

The styryl dyes deriving from 4-methylpyridine have as quaternizing group, methyl (dye **31**), carboxymethyl (dye **18**) and hexadecyl (dye **15**). Their spectra appear in



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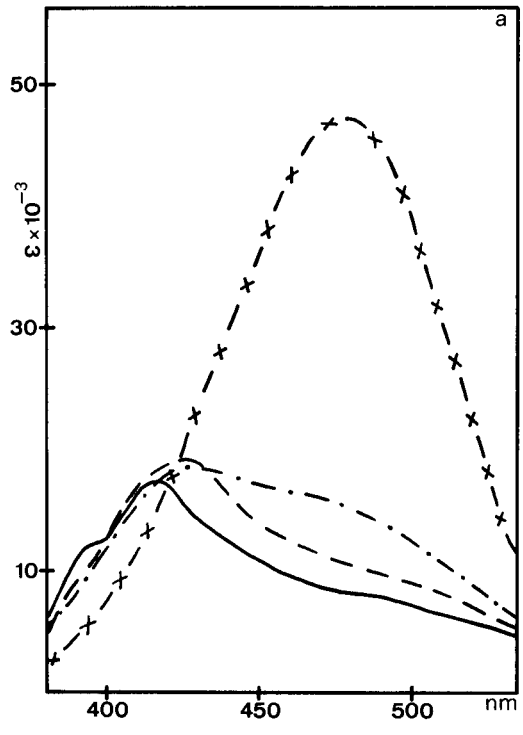
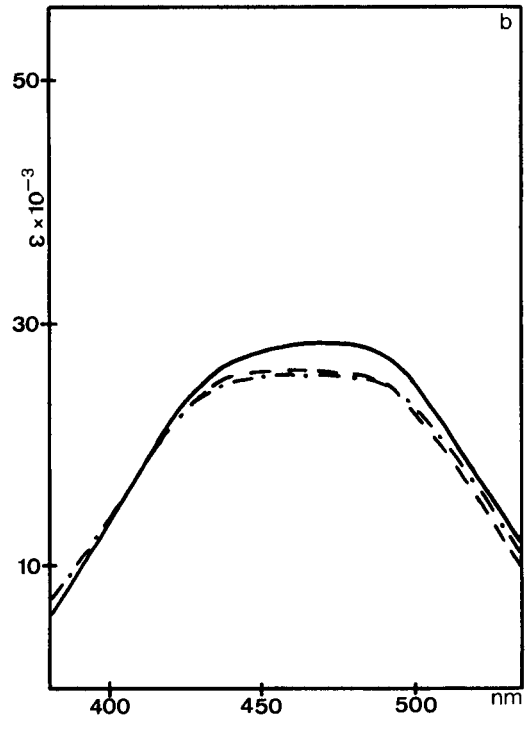
Figures 3, 4 and 5. Insofar as the behaviour in water is concerned, the dye **18** (Figure 4a) absorbs at short wavelengths compared to the alcohol solution and its aggregation is unchanged, in the examined concentration range; the absorption curves are practically superimposable,





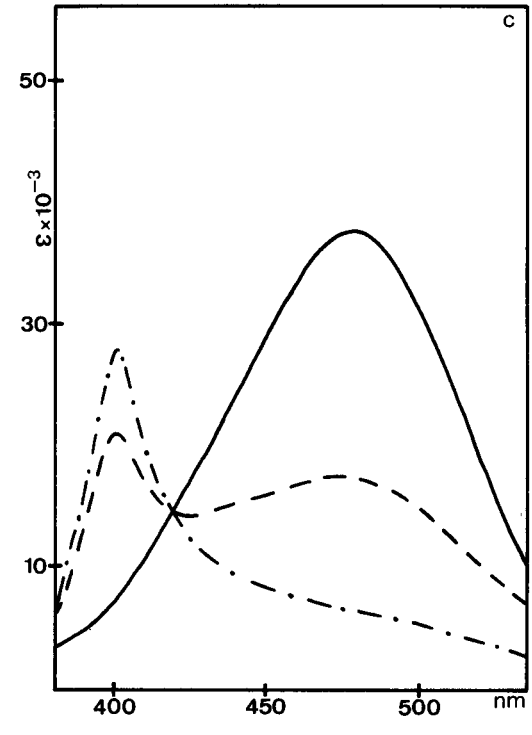
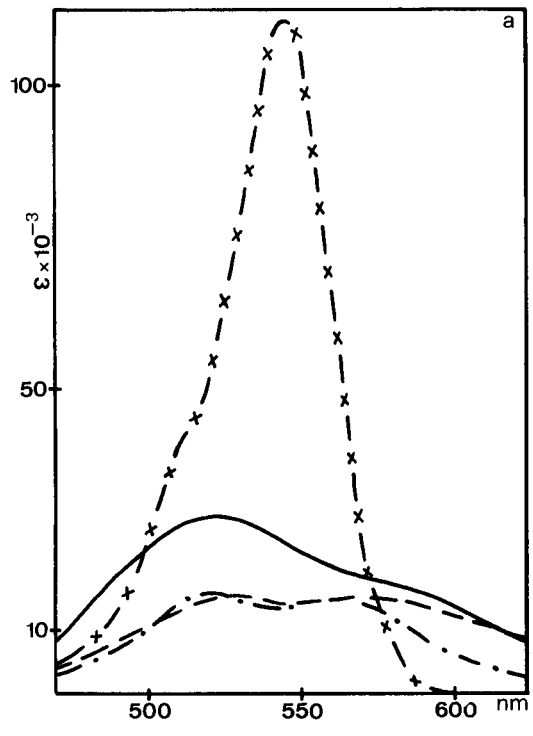
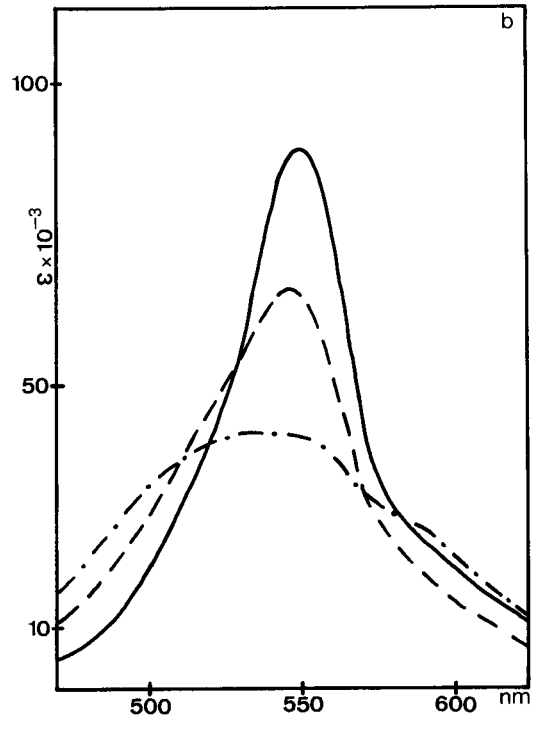


Figure 5. Spectra of dye n. **15**.
a -x-x- in methanol ($1 \times 10^{-5}M$); -•-•- in water ($0.5 \times 10^{-5}M$); --- in water ($1 \times 10^{-5}M$); — in water ($2 \times 10^{-5}M$).
b fixed cyanine ($2 \times 10^{-5}M$); variable SDS: — ($80 \times 10^{-3}M$); --- ($8 \times 10^{-3}M$); -•-•- ($4 \times 10^{-3}M$).
c fixed cyanine ($2 \times 10^{-5}M$); variable HTAB: — ($7 \times 10^{-3}M$); --- ($7 \times 10^{-4}M$); -•-•- ($7 \times 10^{-6}M$).

while the dye **31** (Figure 3a) shows an apparent lowering of the molar extinction coefficients as the concentration increases. The long chain dye **15** displays absorptions at short wavelengths (Figure 5a), more sensitive to concentration changes; the band near 390 nm is tentatively assigned to a complex aggregate system of 'H' type. The anionic surfactant (SDS), if added above its cmc, highly deaggregates the short chain dyes while, at the lowest concentration, the behaviour of these dyes is nearly the same as in the aqueous media (Figures 3b and 4b). The very broad spectrum of the long chain dye (Figure 5b) indicates, in addition to the monomer, the co-existence of various aggregates; the SDS, even when added in small amounts, markedly changes the patterns of the aqueous solutions and, above its cmc, weakly promotes the formation of the





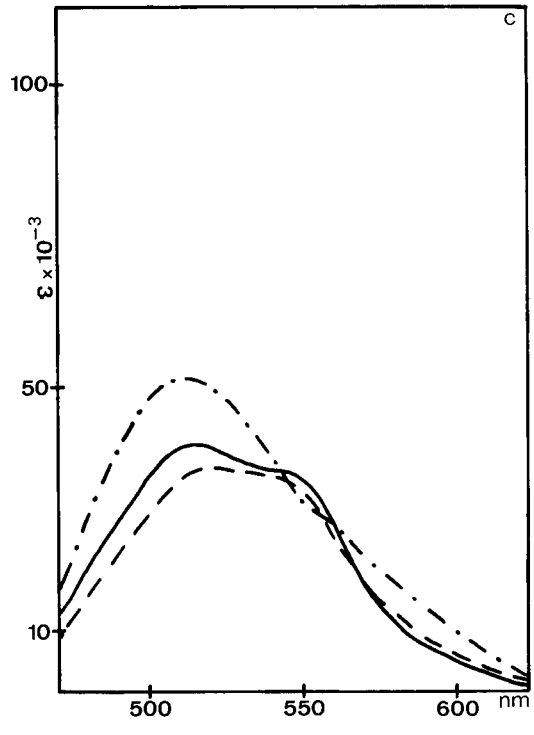
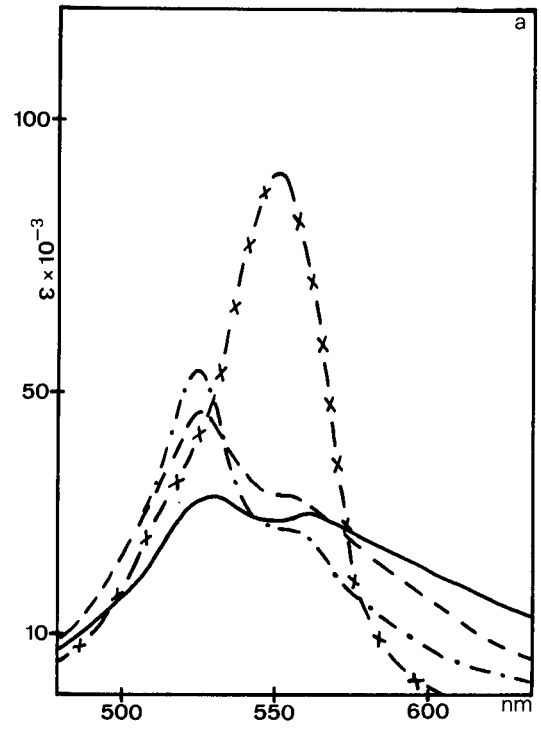
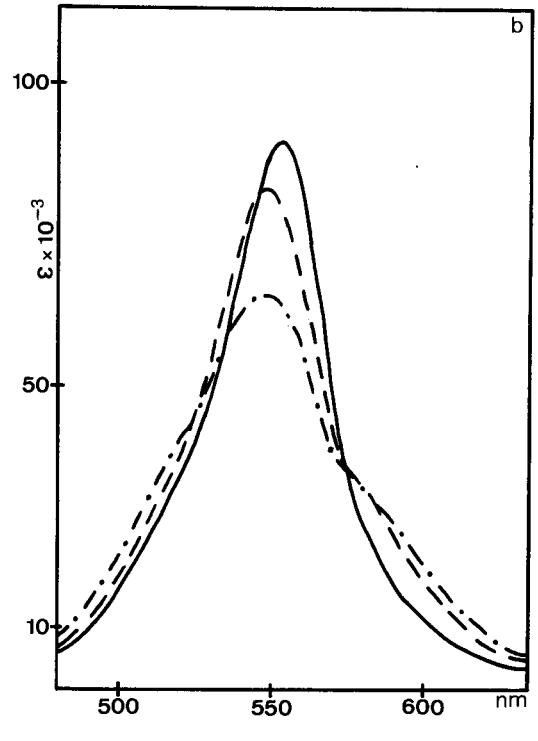


Figure 6. Spectra of dye n. **21**.
a -x-x- in methanol ($1 \times 10^{-5}M$); -•-•- in water ($0.5 \times 10^{-5}M$); --- in water ($1 \times 10^{-5}M$); — in water ($2 \times 10^{-5}M$).
b fixed cyanine ($2 \times 10^{-5}M$); variable SDS: — ($80 \times 10^{-3}M$); --- ($8 \times 10^{-3}M$); -•-•- ($4 \times 10^{-3}M$).
c fixed cyanine ($2 \times 10^{-5}M$); variable HTAB: — ($7 \times 10^{-3}M$); --- ($7 \times 10^{-4}M$); -•-•- ($7 \times 10^{-6}M$).

monomeric species. The cationic surfactant appears to have little, if any, effect on dyes **31** and **18** (Figures 3c and 4c) whereas it deaggregates strongly dye **15** in which, above the cmc of the surfactant, a clear absorption at 477 nm appears (Figure 5c), as noted in alcohol media. Moreover, an isosbestic point is distinctly discernible.

The spectra of dyes **21** ('meso' methyl dye with C_{12} chains), **23** ('meso' ethyl dye with C_{16} chains) and **25** (symmetrical dye with 2-quinoline nuclei and C_{16} chains) are reported in Figures 6, 7 and 8 respectively. In aqueous media these hydrophobic dyes show complex aggregations (Figures 6a, 7a, 8a) connected to absorptions covering a large portion of the visible spectrum. The SDS is very effective in the formation of the monomeric form of the 'meso' dyes **21** and **23** (Figures 6b and 7b). In the case of dye **25** (Figure 8b) the spectrum presents again the situa-





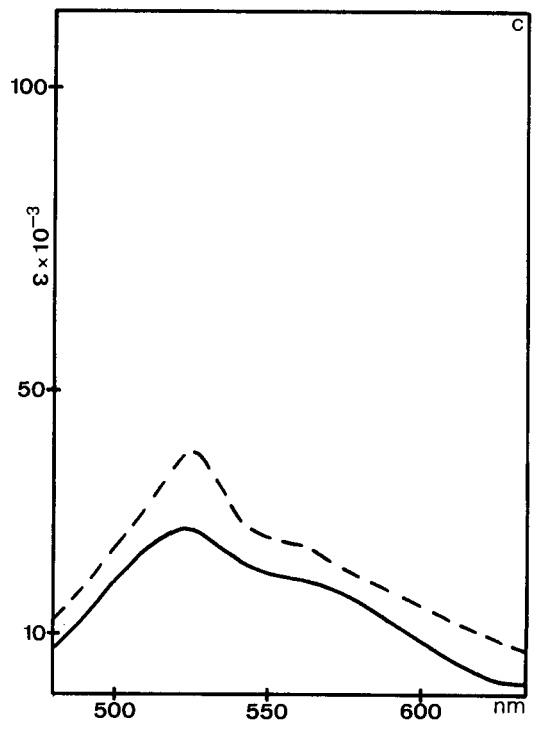
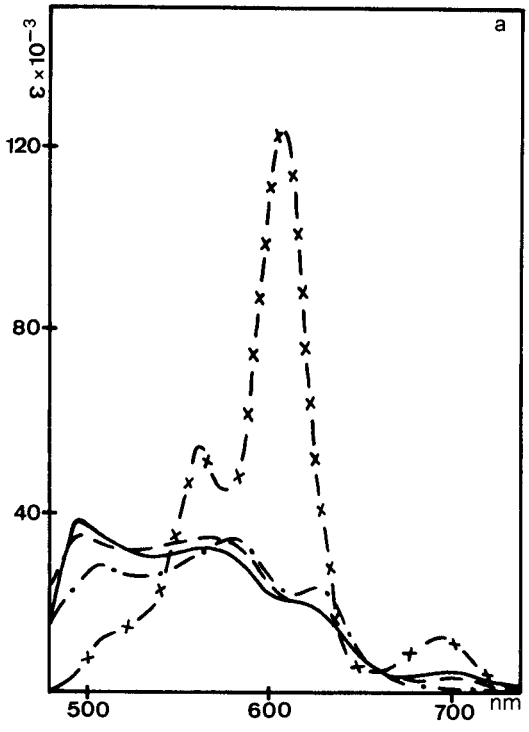
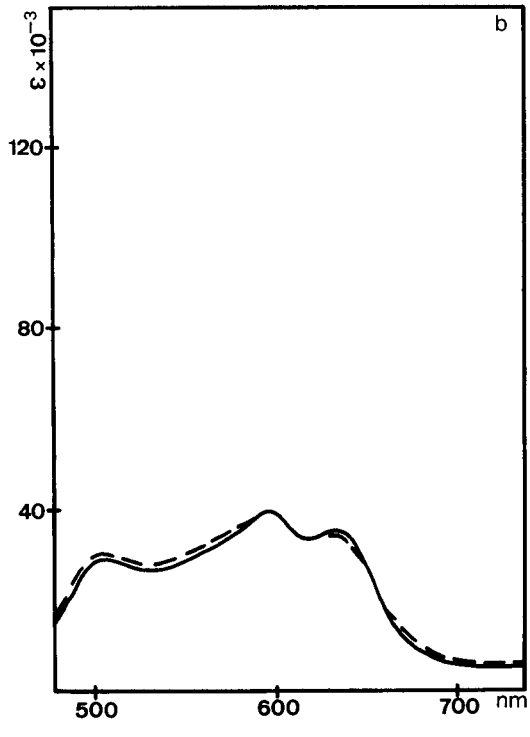


Figure 7. Spectra of dye n. **23**.
a -x-x- in methanol ($1 \times 10^{-5}M$); -•-•- in water (0.25×10^{-5} *M*); --- in water ($0.5 \times 10^{-5}M$); — in water ($1 \times 10^{-5}M$).
b fixed cyanine ($2 \times 10^{-5}M$); variable SDS: — (80×10^{-3} *M*); --- ($8 \times 10^{-3}M$); -•-•- ($4 \times 10^{-3}M$).
c fixed cyanine ($2 \times 10^{-5}M$); variable HTAB: — (7×10^{-3} *M*); --- (7×10^{-6} and $7 \times 10^{-4}M$ superimposed).

tion observed in aqueous media, namely the co-existence of aggregate and monomeric species with a prevalence of the latter. Only two curves are drawn due to the precipitation of the dye at the lowest concentration of the surfactant. The effect of HTAB is quite surprising. Whilst in the case of dye **15** a strong deaggregating effect was observed, the opposite effect is shown by dyes **21** and **23**: in Figures 6c and 7c the enchanced formation of high aggregates is evidenced by the general strengthening of the short wavelength bands. The dye **25** (Figure 8c) closely reproduces the situation observed in the presence of SDS, except for the precipitation. For comparison purposes, in Figure 9, the spectra of the counterpart of dye **25**, having a C_1 instead of a C_{16} chain, are reported. Such a dye has been previously studied [13] in the presence of vesicles and of SDS. Here we now present the spectra in the presence of





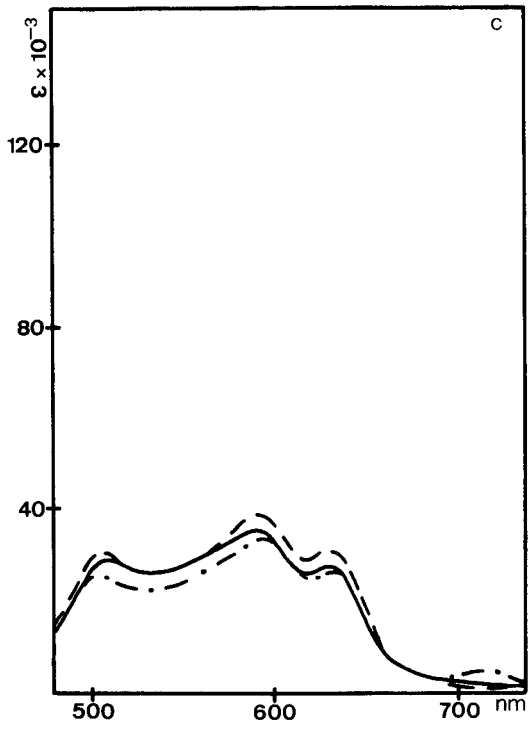


Figure 8. Spectra of dye n. **25**.
a -x-x- in methanol ($1 \times 10^{-5}M$); -•-•- in water ($0.5 \times 10^{-5}M$); --- in water ($1 \times 10^{-5}M$); — in water ($2 \times 10^{-5}M$).
b fixed cyanine ($1 \times 10^{-5}M$); variable SDS: — ($80 \times 10^{-3}M$); --- ($8 \times 10^{-3}M$); [precipitation of the dye at $4 \times 10^{-3}M$].
c fixed cyanine ($1 \times 10^{-5}M$); variable HTAB: — ($7 \times 10^{-3}M$); --- ($7 \times 10^{-4}M$); -•-•- ($7 \times 10^{-6}M$).

HTAB. The behaviour is similar to that observed in aqueous media; *i.e.* monomeric and dimeric species exist with a prevalence of the first.

In conclusion, we observe that the presence of long alkyl chains is accompanied by the formation of several aggregates (except for the 'J' type) in aqueous solutions, easily detectable by their spectra. It being understood that individual cases must be examined, the more effective deaggregating effect of the anionic surfactant (SDS) especially towards short chain structures, must be noted.

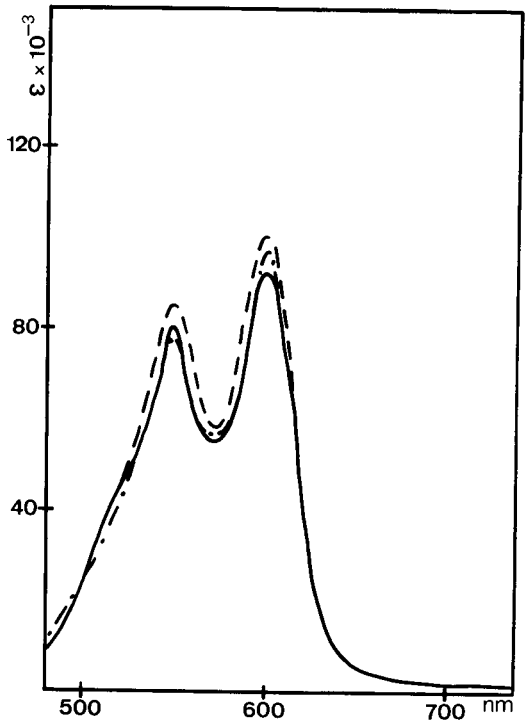


Figure 9. Spectra of 2-[3-(1-methyl-2-quinolynilydene)-propenyl]-1-methylquinolinium iodide (ref 13) (2×10^{-5} *M*); variable HTAB: — (7×10^{-3}*M*); ---(7×10^{-4}*M*); -•-•- (7×10^{-6}*M*).

EXPERIMENTAL

The nmr spectra were obtained with a Varian T 60 spectrometer in DMSO-d_6 solution (6%) using TMS as internal standard. Electronic spectra were recorded on a Unicam SP 8-100 spectrophotometer on freshly prepared solutions. The R_f values were determined on silica gel 60 F-254 tlc plates (Merck), using as eluent B.A.W. (butanol:acetic acid:water) 4:1:5. For dyes **25, 26, 27** cellulose F tlc plates (Merck) and chloroform:-ethanol 4:1 were used.

In Tables 1-3 the structures and some data related to the synthesis and to the characterization of salts and dyes are reported. Further details on the preparations of individual compounds are reported below. All the crude precipitates were slurried with anhydrous ether before the crystallization. All the analytical specimens gave a single spot on tlc.

Salts **1, 2, 3, 4, 6, 7, 9, 10, 11, 12**.

The heteroaromatic bases (1.0 mole) were refluxed with suitable alkyl halides (0.8 moles) for 6 hours (alkyl iodides) and 12 hours (alkyl chlorides).

Salts **5** and **8**.

4-Methylpyridine and 2-methylbenzothiazole respectively (1.0 mole) were refluxed at 170° on an oil bath with monochloracetic acid (1.2 moles) for 30 minutes (salt **5**) and 7 hours (salt **8**).

Dyes **13, 15, 17, 18**.

A solution of the suitable salt (10^{-2} moles) in 15 ml of absolute ethanol (piperidine as catalyst) and *p*-dimethylaminobenzaldehyde (1.4×10^{-2} moles) were refluxed for 45 minutes.

Dye **14**.

Perchloric acid 70% (4 ml) was dropped into a solution of dye **13** (4×10^{-3} moles) in 100 ml of glacial acetic acid. To the bleached solution 2 litres of distilled water were added.

Dye **16**.

A solution of dye **15** (4×10^{-3} moles) in 25 ml of ethanol was mixed with a solution of silver nitrate (4×10^{-3} moles) in 5 ml of ethanol. The mixture was kept in the dark at 40° for 15 minutes, the solid silver iodide was filtered off and the solution was reduced to 5 ml under vacuum.

Dyes **19, 20**.

The suitable quaternary salts (10^{-2} moles) and *p*-dimethylaminobenzaldehyde (1.5×10^{-2} moles) in 20 ml of acetic anhydride were refluxed for one hour.

Dye **21**.

A solution of **6** (4×10^{-2} moles) in 20 ml of acetic anhydride and triethylorthoacetate (8×10^{-2} moles) were refluxed for 2 hours. The mixture was kept overnight at 0°.

Dye **22**.

Dye **21** was treated with the same procedure followed in the preparation of dye **14**.

Dyes **24, 25, 26**.

A solution of quaternary salt (5×10^{-3} moles) in 5 ml of pyridine and triethylorthoformate (10^{-2} moles) were refluxed for 4 hours (dyes **24** and **25**) and 12 hours (dye **26**). The mixture was kept 24 hours at 0°.

Dye **27**.

A solution of **10** (2×10^{-3} moles) in 8 ml of nitrobenzene and triethylorthoformate (4×10^{-3} moles) were refluxed for 30 hours. The mixture was kept at 5° for 72 hours.

Dye **28**.

A solution of **11** (4.5×10^{-2} moles) and of *N,N*-diphenylformamidine (9×10^{-2} moles) in 60 ml of acetic anhydride was refluxed for one hour. The crude 4-(β-acetylanilinovynyl)-1-hexadecylquinolinium bromide was well slurried in ether and its solution (6×10^{-3} moles) in 8 ml of absolute ethanol was treated with **7** (6×10^{-3} moles) with triethylamine (10^{-2} moles). After refluxing 2 hours, the mixture was kept overnight at 0°, filtered and the product washed with ether. The bromide was converted into the perchlorate treating a solution of the dye in ethanol with a saturated aqueous solution of potassium perchlorate.

Dye **29**.

A solution of 2-(β-acetylanilinovynyl)-3-hexadecylbenzothiazolium iodide [6] (3.5×10^{-3} moles), **9** (3.5×10^{-3} moles), triethylamine (5×10^{-3} moles) in 7 ml of ethanol was refluxed for one hour. The mixture was kept overnight at −10°. The crude product was washed with ether and converted with perchloric acid according to the procedure followed in the preparation of dye **14**.

Ketone **30** (3-Hexadecyl-2-(propionylmethylidene)benzothiazoline).

The general procedure indicated in [15] was followed. Propionylchloride (1.2×10^{-3} moles) was dropped into a solution of **7** (0.8×10^{-3} moles) in 200 ml of anhydrous pyridine at −5°. Triethylamine (5 ml) was then added. The mixture was kept for 2 hours at room temperature, then for 3 hours at 100°. The hot mixture was put into one litre of iced water and the *p*H was adjusted to 6 with hydrochloric acid. After 24 hours the precipitate was collected and washed with water. The dry solid was exhaustively extracted with boiling ligroin, the solvent reduced to small volume and the product collected after 48 hours at 0°. The crude ketone was crystallized from ligroin giving 0.2 g (60%) of pale grey crystals, mp 58-59°. Electronic spectrum reported in Figure 1; ^{1}H-nmr: δ 1.00-2.00 (m, 34 H = 31 H long chain + 3 H methyl of the ethyl group), 2.52 (q, 2 H methylene of the ethyl group), 4.00 (t, broad, 3 H first methylene of the long chain), 5.87 (s, 1 H methine), 6.92-7.67 (m, 4 H aromatic).

Anal. Calcd. for $C_{27}H_{43}NOS$: C, 75.47; H, 10.09; N, 3.26. Found: C, 75.39; H, 10.17; N, 3.31.

Dye **23**.

To a solution of **30** (10^{-2} moles) and phosphorus oxyhloride (3×10^{-2} moles) in 70 ml of anhydrous benzene, kept for 30 minutes at 30°, **7** was added (10^{-2} moles). After a gentle warming, triethylamine (2×10^{-2} moles) was added and the mixture was refluxed for 2 hours. After the reduction to small volume under vacuum, the collected dye was converted with perchloric acid according to the procedure followed in the preparation of dye **14**.

Dye **31**.

The dye was prepared as indicated in reference [16].

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[1] This work was achieved with the contribution of Progetto Finalizzato del CNR Chimica Fine e Secondaria.

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