Assembled Systems [Picoline]-[X-azolopyridine]: Bases, Salts and Polymethine Dyes [1].

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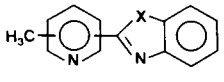
A series of assembled heterocyclic bases containing picolines and X-azolopyridines was synthesized, thus widening the outline of available compounds for a comparison of their chemical, physical and spectroscopic properties. In particular, the competition of three different sites toward quaternizing agents has been explored and individual behaviours have been clarified by ^1H nmr spectroscopy. Styryl dyes have been prepared and characterized. The effect of cationic and anionic surfactants on deaggregating one unsymmetrical cyanine has been successfully tested.

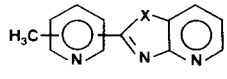
J. Heterocyclic Chem., **27**, 1777 (1990).

Assembled heterocyclic systems kept our attention in recent years. A first set of papers [2-7] has been devoted to describing structures **I**, and the related quaternary salts and polymethine dyes, thus evidencing the combined effects of pyrido and benzazole rings. Similar investigations regarded structures **II**, containing X-azolo[4,5-*b*]pyridine [8,9]. The outline is now widened by additional compounds **II** and new structures **III**, thus allowing a general comparison among structures which differ from each other (i) by the relative positions of the rings, (ii) by the nature of the X heteroatom, or (iii), when X = NH, by the annellation of the imidazopyridine moiety, *i.e.* [4,5-*b*] or [4,5-*c*].



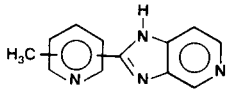
I

X=O, S, NH



II

X=O, NH



III

Results and Discussion.

The bases have been synthesized following the pathway indicated below. Table 1 reports physical and spectroscopic data of bases **1-7**.

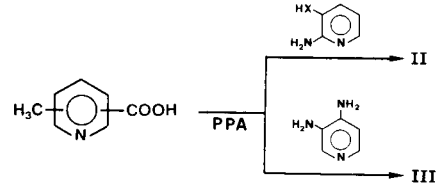
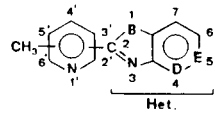


Table 1

Characterization Data of Bases



Compound number	CH3 position	Structure Hetaryl position	B	D	E	Crystallization solvent[a]	Mp °C	Rf	Electronic absorption spectra λmax[b] nm	log ε	Empirical Formula	Elemental Analyses Calcd./Found C	H	N
1	4'	2'	NH	CH	N	F	295-6	0.26	297	4.36	$C_{12}H_{10}N_4$	68.56	4.79	26.65
												68.60	4.81	26.59
2	6'	2'	NH	CH	N	G	207-8	0.30	300	4.37	$C_{12}H_{10}N_4$	68.56	4.79	26.65
												68.53	4.78	26.67
3	4'	3'	NH	CH	N	F	237-9	0.26	281	4.16	$C_{12}H_{10}N_4$	68.56	4.79	26.65
												68.68	4.80	26.50
4	6'	3'	NH	CH	N	L	250-1	0.32	294	4.36	$C_{12}H_{10}N_4$	68.56	4.79	26.65
												68.50	4.81	26.57
5	2'	4'	NH	CH	N	L	227-9	0.31	291	4.24	$C_{12}H_{10}N_4$	68.56	4.79	26.65
												68.63	4.85	26.58
6	2'	4'	NH	N	CH	L	263-5	0.62	312	4.42	$C_{12}H_{10}N_4$	68.56	4.79	26.65
												68.51	4.89	26.65
7	2'	4'	O	N	CH	L	158-9	0.65	306	4.42	$C_{12}H_9N_3O$	68.24	4.29	19.89
												68.31	4.32	19.77

[a] F=Ethanol, G=Water, L=Acetonitrile.

[b] The λ_{max} and log ε values correspond to the most intense peak of the long-wavelenth band.

Figure 1 has been drawn for an extensive comparison of the melting points of compounds having the general formulas **I, II, III**. Two trends are observed, *i.e.* (i) benzoxazole derivatives have the lowest melting points, (ii) compounds containing the oxazolo[4,5-*b*]pyridine moiety melt at higher temperatures than their benzoxazole counterparts, but at lower temperatures than all the remainder, (iii) the imidazole moiety increases the melting points, depending both on the assembled ring and the mutual position of the heteroaromatic and methyl substituents.

An analogous general comparison is usually established also for chromatographic data, as shown in Figure 2.

As a general trend, compounds with the greatest retention by the polar substrate are those containing the imidazo-[4,5-*c*]pyridine system, followed by the [4,5-*b*] analogs, and by those containing the benzimidazole, the pyridoxazole, and the benzoxazole rings. This behaviour agrees with the greater polarity of a condensed pyridine ring versus a condensed benzene ring and with the greater polarity and the

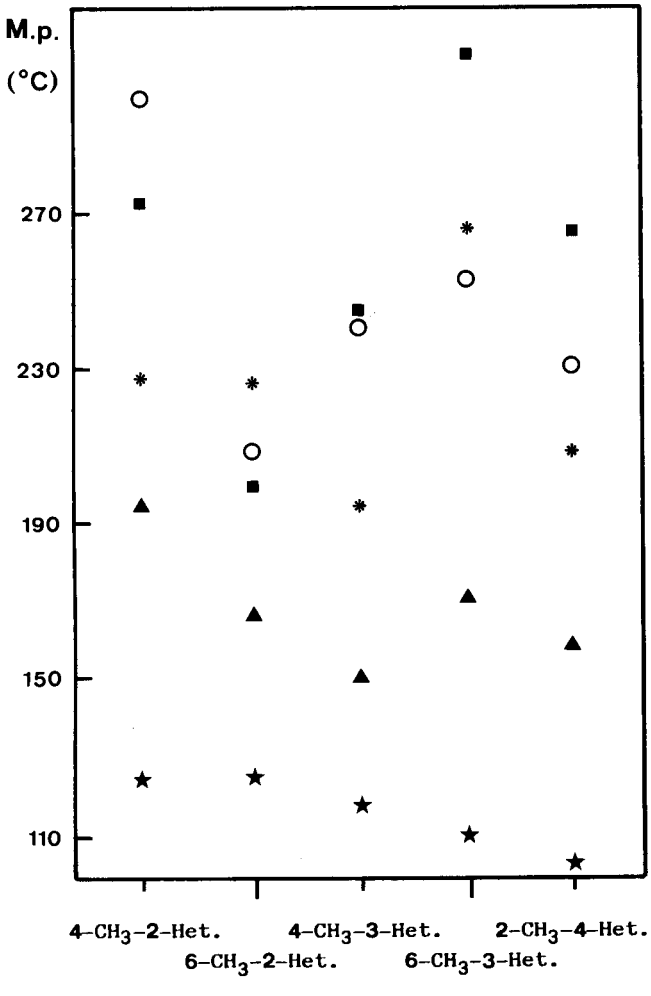


Figure 1. Comparison of Melting Points of compounds **I-IV**. Hetaryl: ○ 2-imidazo[4,5-*c*]pyridyl, ■ 2-imidazo[4,5-*b*]pyridyl, ▲ 2-oxazo[4,5-*b*]pyridyl, * 2-benzimidazolyl, ★ 2-benzoxazolyl.

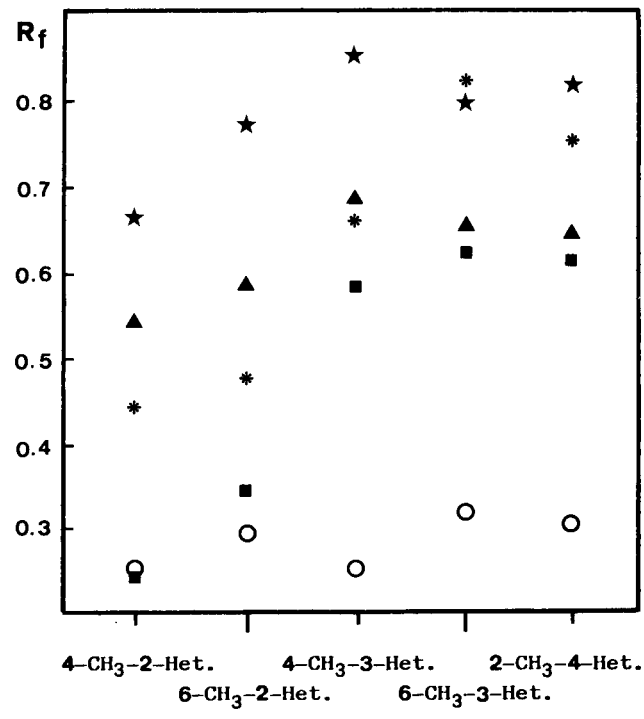


Figure 2. Comparison of Rf values of compounds **I-IV**. For key see Figure 1.

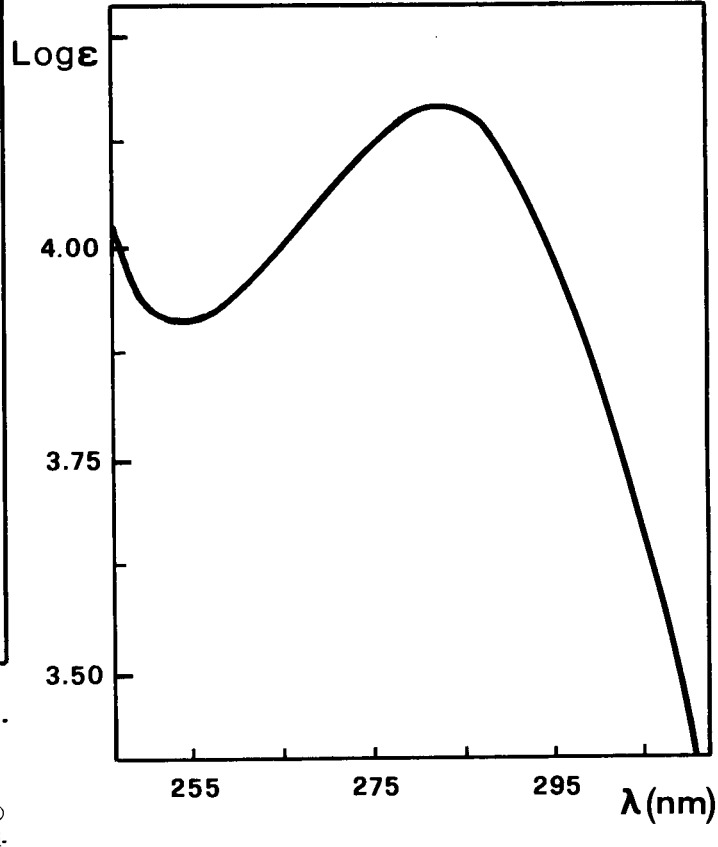


Figure 3. Electronic absorption spectrum of compound **3**

greater hydrogen bonding ability of imidazoles, compared to oxazoles. An important role, could be also played by the tendency to form aggregates, doubtless more marked for imidazole derivatives. In fact, benzimidazole and imidazo[4,5-*b*]pyridine derivatives show a strong enhancement of Rf values going from structures linked to the α-position of the pyridine ring to those linked to β or γ positions. The above effect is, indeed, slightly evident for oxazole derivatives, which aggregate with difficulty, while imidazo[4,5-*c*]pyridines which have a high affinity, exhibit a high state of aggregation.

The electronic spectra of compounds **1-7** show the general pattern reported in Figure 3 for compound **3**, chosen as an example. The long-wavelength band, probably due to a pyridylideneimino chromogen [9], lie in the range 280-315 nm. Figure 4 summarizes the positions of the

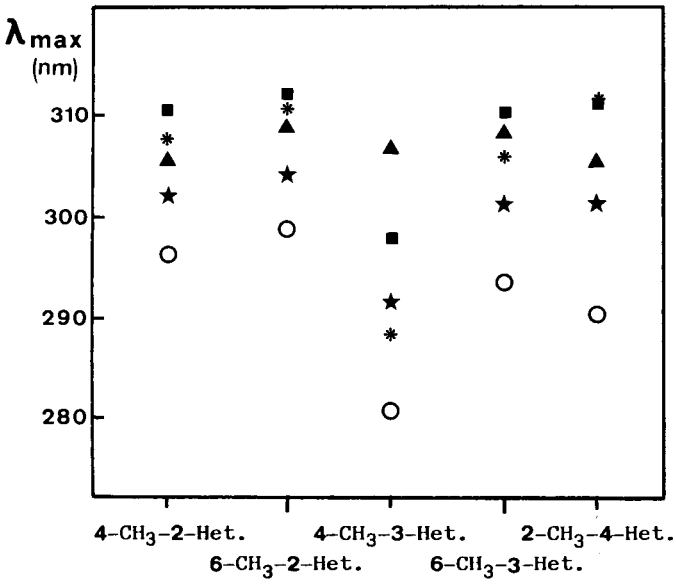


Figure 4. Comparison of λ max of compounds **I-IV**. For key see Figure 1.

maxima for the whole series. So far as imidazoles are concerned, the maxima are shifted towards the long wavelengths according to the sequence: imidazo[4,5-*b*]pyridine > benzimidazole > imidazo[4,5-*c*]pyridine. In the oxazole series, the change *benzo* → *pyrido* is accompanied by a bathochromic shift. As far as the relative positions of groups are concerned, referring to the *picoline* ring, if the methyl is in the γ position and the hetaryl in the β position (*vicinal* isomers), marked hypsochromic effects occur in comparison with other isomers in which the perturbation caused by *vicinal* groups is absent. The absorption intensities, plotted in Figure 5, have the same general trend as the position of the maxima. In particular, it is worth mentioning the hypochromic effect is due to the imidazo[4,5-*c*]-pyridine, and the hyperchromic effect is due to the [4,5-*b*]

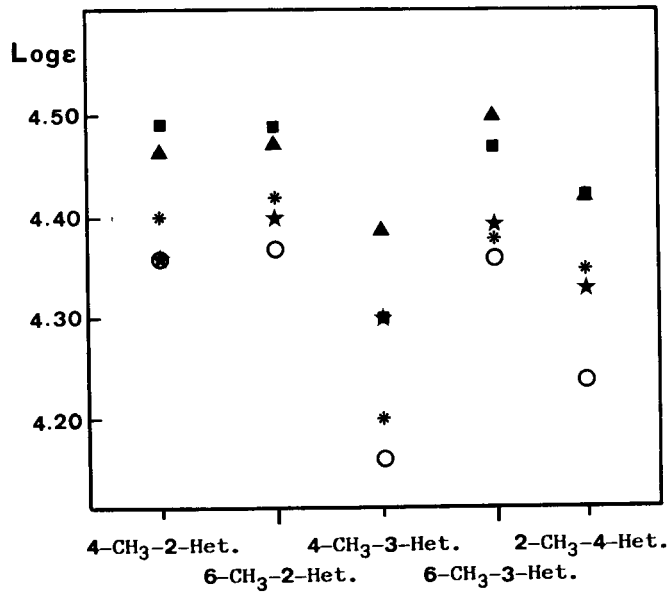


Figure 5. Log ε values of compounds **I-IV**. For Key see Figure 1.

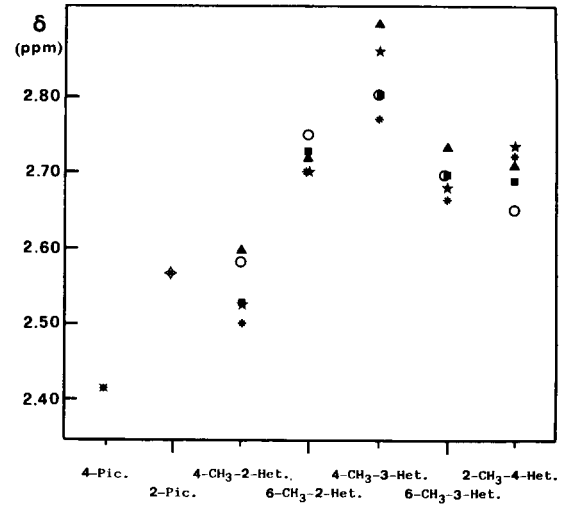


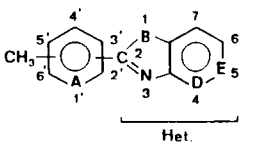
Figure 6. Methyl protons chemical shifts of compounds **I-IV**. For Key see Figure 1.

isomer.

The ^{1}H nmr spectra have been recorded, and chemical shift values are collected in Table 2. The assignments are easy because of the large accumulation of data collected on this family of heterocyclics. All of the spectra are of high quality and the data sustain the assigned structures. The simplest structure-chemical shift correlation regards the methyl-protons and is drawn in Figure 6 in which, the unsubstituted picolines have also been included. The linking of an X-azolyl to the pyridine ring exerts a systematic deshielding of the methyl-protons, which attains a maxi-

Table 2

Proton Chemical Shifts (δ, ppm) of Bases and Salts

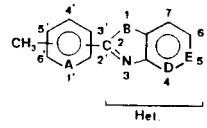


Compound number	CH_3 position	Structure Hetaryl position	A	B	D	E	Proton Number 2'	3'	4'	5'	6'	4'CH_3[a] (γCH_3)	6'CH_3[a] (αCH_3)	1'+NCH_3	4	5	6	7	4+NCH_3	5+NCH_3
1	4'	2'	N	NH	CH	N		8.27		7.42	8.63	2.48			9.01		8.37	7.57		
2	6'	2'	N	NH	CH	N		8.20	7.89	7.40			2.65		9.00		8.34	7.60		
3	4'	3'	N	NH	CH	N	8.97			7.47	8.57	2.70			9.00		8.37	7.65		
4	6'	3'	N	NH	CH	N	9.33		8.47	7.50			2.60		9.02		8.38	7.67		
5	2'	4'	N	NH	CH	N		7.99		7.92	8.61		2.55		8.99		8.31	7.61		
6	2'	4'	N	NH	N	CH		8.02		7.95	8.62		2.59			8.41	7.26	8.04		
7	2'	4'	N	O	N	CH		8.02		7.96	8.73		2.61			8.63	7.54	8.32		
8	4'	2'	N	NH	CH	+NCH_3		8.31		7.55	8.72	2.51			9.57		8.67	8.10		4.47
9	6'	2'	N	NH	CH	+NCH_3		8.20	7.95	7.50			2.65		9.50		8.60	8.07		4.45
10	4'	3'	+NCH_3	NH	CH	+NCH_3	9.72			8.23	9.05	2.95		4.50	9.49		8.72	8.35		4.45
11	6'	3'	+NCH_3	NH	CH	+NCH_3	9.85		9.14	8.36			2.93	4.48	9.68		8.74	8.37		4.42
12	2'	4'	+NCH_3	NH	CH	+NCH_3		8.77		8.59	9.23		2.95	4.34	9.65		8.62	8.27		4.46
13	2'	4'	+NCH_3	NH	+NCH_3	CH		8.79		8.64	9.21		2.93	4.33		8.92	7.85	8.86	4.53	
14	2'	4'	+NCH_3	O	N	CH		8.80		8.61	9.26		3.01	4.40		8.72	7.66	8.39		
15	4'	2'	N	NH	CH	+NC_6H_{13}		8.30		7.56	8.72	2.52			9.69		8.83	8.15		4.75
16	4'	2'	N	NH	CH	+NC_8H_{17}		8.30		7.56	8.72	2.52			9.69		8.83	8.15		4.75
17	6'	2'	N	NH	CH	+NC_6H_{13}		8.29	8.02	7.57			2.68		9.70		8.84	8.17		4.74

[a] α and γ are referred to the usual positions in the pyridine ring.

Table 3

Characterization Data of Quaternary Salts



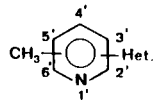
Compound number	CH_3 position	Structure Hetaryl position	A	B	D	E	Crystallization solvent[a]	Mp °C	Rf	Electronic absorption spectra λ_{max}[b] nm	log ε	Empirical Formula	Elemental Analyses Calcd./Found C	H	N
8	4'	2'	N	NH	CH	+NCH3	F	272-3	0.18	299	4.36	$C_{13}H_{13}IN_4$	44.34	3.72	15.91
													44.39	3.67	15.85
9	6'	2'	N	NH	CH	+NCH3	L	252-4	0.19	303	4.38	$C_{13}H_{13}IN_4$	44.34	3.72	15.91
													44.27	3.78	15.86
10	4'	3'	+NCH3	NH	CH	+NCH3	F	230-3	0.02	295	4.22	$C_{14}H_{16}I_2N_4$	34.03	3.26	11.34
													33.96	3.31	11.37
11	6'	3'	+NCH3	NH	CH	+NCH3	F	255-7	0.01	301	4.34	$C_{14}H_{16}I_2N_4$	34.03	3.26	11.34
													34.11	3.25	11.28
12	2'	4'	+NCH3	NH	CH	+NCH3	F	224-7	0.01	320	4.36	$C_{14}H_{16}I_2N_4$	34.03	3.26	11.34
													34.06	3.28	11.30
13	2'	4'	+NCH3	NH	+NCH3	CH	F	258-61	0.03	358	4.47	$C_{14}H_{16}I_2N_4$	34.03	3.26	11.34
													34.13	3.21	11.32
14	2'	4'	+NCH3	O	N	CH	F	263-4	0.06	328	4.35	$C_{13}H_{12}IN_3O$	44.21	3.42	11.90
													44.25	3.46	11.87
15	4'	2'	N	NH	CH	+NC8H13	M	152-4	0.44	300	4.39	$C_{18}H_{23}IN_4$	51.19	5.49	13.27
													51.14	5.54	13.29
16	4'	2'	N	NH	CH	+NC8H17	M	154-7	0.48	300	4.38	$C_{20}H_{27}IN_4$	53.34	6.04	12.44
													53.38	6.01	12.40
17	6'	2'	N	NH	CH	+NC8H13	Q	167-70	0.43	303	4.38	$C_{18}H_{23}IN_4$	51.19	5.49	13.27
													51.21	5.43	13.32

[a] F=Ethanol, L=Acetonitrile, M=Acetone, Q=Acetone/Ethyl ether.

[b] The λ_{max} and log ε values correspond to the most intense peak of the long-wavelenth band.

Table 4

Effect of quaternization on chemical shifts of methyl protons (Δ δ C-CH_3)[a]



Position Methyl	Position Hetaryl	Type of hetaryl[b] R	S	T	W	Z
4'	2'	0.03	0.10	0.03	0.14	0.32
6'	2'	0.00	0.07	0.08	0.08	0.40
4'	3'	0.25	0.33	0.30	0.26	0.32
6'	3'	0.35	0.35	0.32	0.31	0.36
2'	4'	0.40	0.34	0.40	0.28	0.31

[a] Δδ C-CH_3=δC-CH_3(salt)-δC-CH_3(base) in ppm.

[b] The structures are referred to the starting bases:

R=2-imidazo[4,5-c]pyridyl

S=2-imidazo[4,5-b]pyridyl

T=2-oxazo[4,5-b]pyridyl

W=2-benzimidazolyl

Z=2-benzoxazolyl

mum in the 4'-methyl-3'-X-azolyl systems. This is in agreement with, (i) the general electron attracting effect of both benz-X-azolyls and pyrido-X-azolyls, (ii) the prevalence of an inductive component evidenced by stronger effects when the relative positions of methyls and X-azolyls are *ortho*.

An interesting feature of the present series is the behaviour towards quaternizing agents, due to the possible competition of three sites, *i.e.* a *picoline*, a *pyridine* and an *azole* nitrogen. By reaction with methyl iodide the bases **1-7** have been transformed into quaternary salts **8-14**. A non-systematic test with longer chain iodides led also to the formation of salts **15-17**. The ^1H nmr data of salts **8-17** are presented in Table 2, whereas Table 3 reports other spectroscopic and characterization data. Once more it is worth confirming ^1H nmr efficiency in establishing the structures of the salts, together, obviously, with elemental analyses. When, by quaternization of an azine nitrogen, a positive charge is carried by a pyridine ring, both aromatic and methyl-protons of that ring are strongly shifted downfield in comparison with the related bases. Bis-quaternary salts show two distinct signals (integration 3) in the resonance range of +N-methyl protons. For an easier evaluation of the deshielding effect of quaternization on the

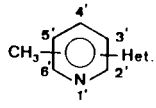
C-methyl-protons, Table 4 has been constructed, which reports $\Delta\delta$ values. It can be seen that, when the hetaryl is linked at the α-position, important deshielding effects are shown only by the benzoxazole derivative, indicating that in this compound quaternization occurred at the *picoline* nitrogen. Similar effects are observed for all hetaryls in β or γ positions. From the above and data in Table 2 and on the basis of our previous experience, we can now draw some general conclusions on quaternization. Systems containing oxazolo[4,5-*b*]pyridine give monoquaternary salts at the *picoline* nitrogen, except that the hetaryl is linked to the α-position. Systems with an imidazopyridine linked to the α position of the picoline ring give monoquaternary salts at the *pyridine* nitrogen; when imidazo[4,5-*b*] or [4,5-*c*]pyridines are linked to the β or γ positions of the picoline ring, both *picoline* and *pyridine* nitrogens react to give *bis*-quaternary salts.

Table 5 shows the effect of quaternization on electronic spectra, in terms of $\Delta\lambda$ max ($\Delta\lambda$ max = λ max salt - λ max base). The effect is, more or less markedly, bathochromic, except for two benzimidazole derivatives. Indeed, these are the 1,3-dimethylbenzimidazolium salts previously described [10,11], in which the two alkyls near to the inter-annular link cause a distorsion of the molecule and a loss of conjugation. The highest $\Delta\lambda$ max values occur in the second column of Table 5 (imidazo[4,5-*b*]pyridines] and in the last line (2'-methyl-4'-hetaryl).

When *picolinium* salts have been available, thanks to the enhanced reactivity of 2' or 4' methyl groups towards *p*-dimethylaminobenzaldehyde, the corresponding styryl dyes of the general formula **IV** have been prepared. Individual formulas and characterization data of the dyes are reported in Table 6. Taking as a reference the absorption maxima of styryl dyes from unsubstituted picolines, the effects of hetaryls (or of hetarylium) can be expressed in terms of $\Delta\lambda$ max ($\Delta\lambda$ max is the difference between λ max of styryl dyes in Table 6 and λ max of the corresponding

Table 5

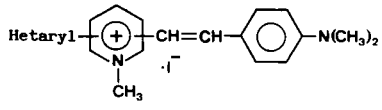
Effect of quaternization on λ_{max} ($\Delta\lambda_{max}$)[a]



Position		Type of Hetaryl[b]				
Methyl	Hetaryl	R	S	T	W	Z
4'	2'	2	29	16	-24	29
6'	2'	3	30	12	-24	30
4'	3'	14	36	5	16	17
6'	3'	7	28	3	11	8
2'	4'	29	46	22	50	34

[a] $\Delta\lambda_{max} = \lambda_{max}$ (salt) - λ_{max} (base) in nm.

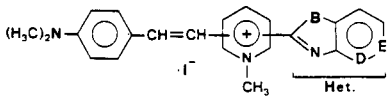
[b] The structures are referred to the starting bases: for key see Table 4



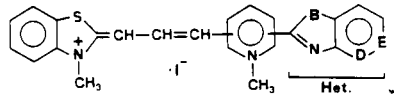
IV

Table 6

Characterization of Cyanine Dyes



Compounds 18-22

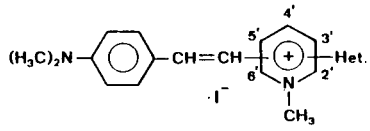


Compound 23

Compound number	Chromogen position	Hetaryl position	B	D	E	Mp °C	Rf	Electronic absorption spectra λ_{max} nm	log ε	Empirical Formula	Elemental Analyses Calcd./Found C	H	N
18	4'	3'	NH	CH	+NCH₃	210-2	0.02	510	4.53	$C_{23}H_{25}I_2N_5$	44.18	4.03	11.20
											44.13	4.11	11.18
19	6'	3'	NH	CH	+NCH₃	235-6	0.05	509	4.76	$C_{23}H_{25}I_2N_5$	44.18	4.03	11.20
											44.22	4.00	11.23
20	2'	4'	NH	CH	+NCH₃	263-6	0.15	504	4.57	$C_{23}H_{25}I_2N_5$	44.18	4.03	11.20
											44.25	3.97	11.16
21	2'	4'	NH	+NCH₃	CH	264-6	0.14	508	4.53	$C_{23}H_{25}I_2N_5$	44.18	4.03	11.20
											44.16	4.08	11.14
22	2'	4'	O	N	CH	246-7	0.24	536	4.50	$C_{22}H_{21}IN_4O$	54.56	4.37	11.57
											54.48	4.41	11.56
23	6'	3'	NH	CH	+NCH₃	243-6	0.02	579	5.14	$C_{24}H_{23}I_2N_5S$	43.20	3.47	10.49
											43.30	3.45	10.42

Table 7

Comparison of spectra of Styryl Dyes ($\Delta\lambda_{max}$)[a]



Position		Type of Hetaryl[b]				
Styryl	Hetaryl	R	S	T	W	Z
4'	2'					51
6'	2'					48
4'	3'	30	32	68	35	55
6'	3'	49	53	81	55	71
2'	4'	44	48	76	48	66

[a] $\Delta\lambda_{max} = \lambda_{max}$ (substituted dye) - λ_{max} (dye from unsubstituted picoline) in nm.

[b] R=imidazo[4,5-c]-N-methylpyridinium-2-yl

S=imidazo[4,5-b]-N-methylpyridinium-2-yl

T=2-oxazo[4,5-b]pyridyl

W=2-benzimidazolyl

Z=2-benzoxazolyl

styryl dye from 2 or 4 picolinium iodides). Table 7 summarizes the $\Delta\lambda$ max values. The presence of the hetaryls promotes consistent bathochromic shifts, mainly due to their electron-withdrawing character.

For completing the comments on parameters reported in Tables 3 and 6, let us consider Rf data. Salts bearing two positive charges are highly retained by the polar substrate. Long alkyl chains, lowering the polarity of salts, enhance Rf values. For analogous reasons styryl dyes are less retained than the parent quaternary salts.

In Table 6, dye **23** is also reported, as an example of an unsymmetrical cyanine. The complete series has not been prepared because cyanine dyes, in contrast to styryl dyes, showed synthetic and purification problems. Styryl dyes **18-22** appear to be practically unaggregated in water as evidenced by spectra of dye **20** reported, as an example, in

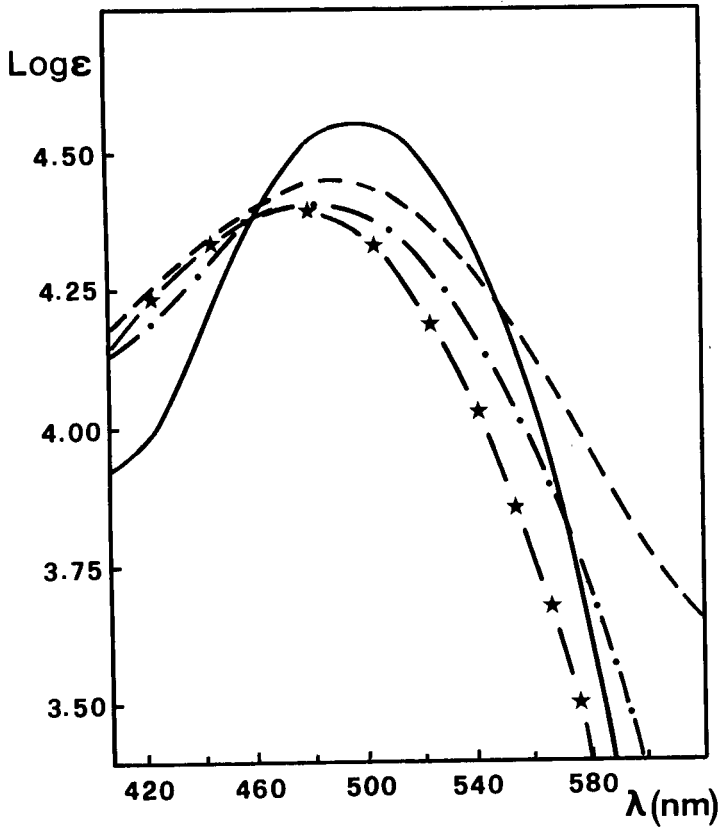


Figure 7. Electronic absorption spectra of dye **20**: — in ethanol, dye concentration $5\cdot10^{-3}$ *M*; in water, dye concentration: ——— $1\cdot10^{-4}$ *M*, —·— $5\cdot10^{-5}$ *M*, —★— $1\cdot10^{-5}$ *M*.

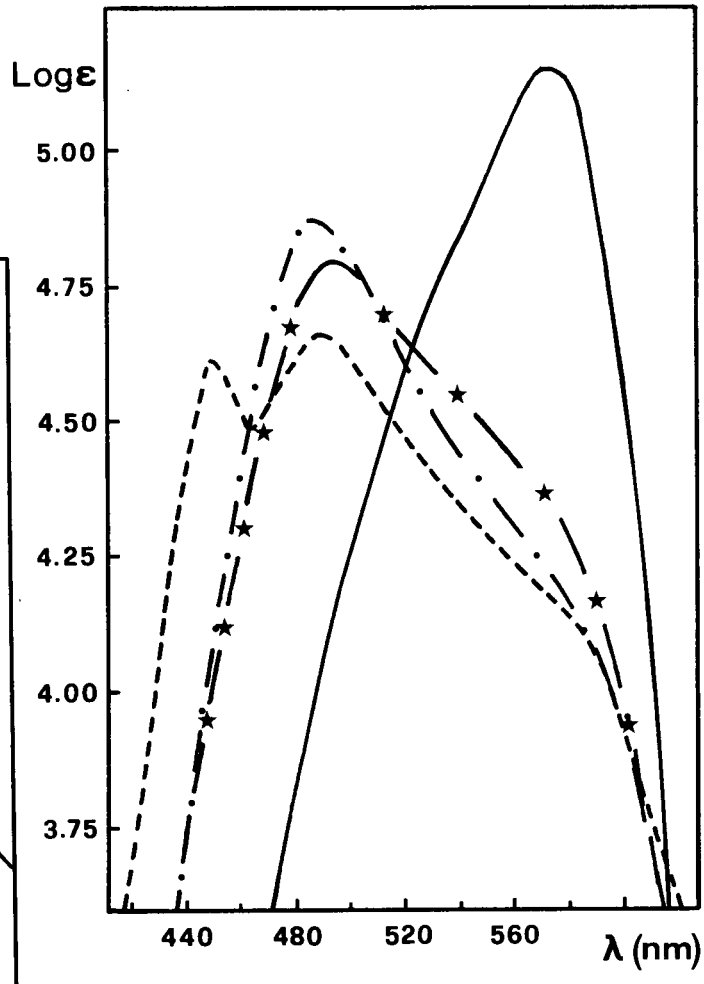


Figure 8. Electronic absorption spectra of dye **23**: — in ethanol, dye concentration $5\cdot10^{-5}$ *M*, in water, dye concentration: ——— $3\cdot10^{-4}$ *M*, —·— $1\cdot10^{-4}$ *M*, —★— $1\cdot10^{-5}$ *M*.

Figure 7. In the explored concentration range, the patterns in water are very close to the pattern in ethanol, where the dye is reasonably in its monomeric state. The

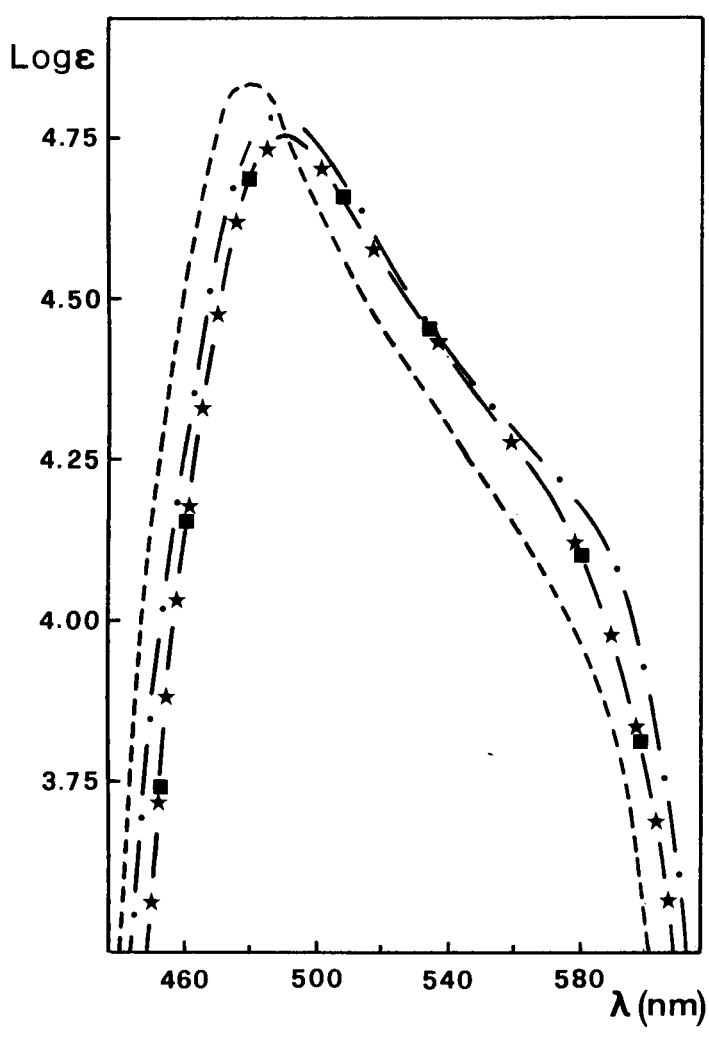


Figure 9. Electronic absorption spectra of dye **23**: concentration $5 \cdot 10^{-5}$ *M*: —■— in water; in water in presence of variable concentration of cetyltrimethylammonium bromide (CTAB): ——— $6 \cdot 10^{-3}$ *M*, —·— $7 \cdot 10^{-4}$ *M* (=CMC), —★— $7 \cdot 10^{-6}$ *M*.

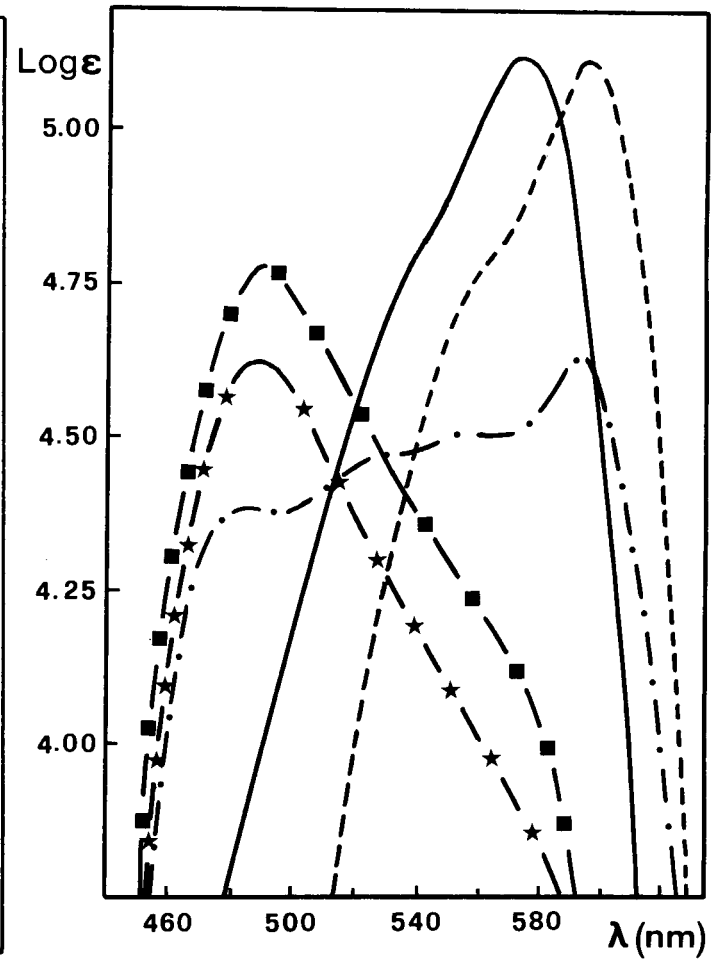


Figure 10. Electronic absorption spectra of dye **23**: concentration $5 \cdot 10^{-5}$ *M*: — in ethanol; —■— in water; in water in presence of variable concentration of sodium dodecylsulphate (SDS): ——— $7 \cdot 10^{-2}$ *M*, —·— $8 \cdot 10^{-3}$ *M* (=CMC), —★— $4 \cdot 10^{-3}$ *M*.

same does not happen for dye **23** which, as shown in Figure 8, displays less intense maxima at shorter wavelengths compared to the ethanolic solution, thus indicating the formation of complex aggregates in water. Being optimum surfactant candidates to promote the deaggregation of dyes [12-14], a cationic surfactant (HTAB, hexadecyltrimethylammonium bromide) and an anionic one (SDS, sodium dodecylsulphate) have been tested at concentrations below, equal and above their cmc (critical micellar concentrations). The results are shown in Figures 9 and 10. If, on one hand, the cationic surfactant appears to be inefficient, on the other, the anionic, from its cmc onwards, promotes the formation of monomeric species, which is evidenced by the peak at *ca.* 599 nm. When the SDS concentration is over the cmc, the absorption at *ca.* 470 nm disappears and the dye attains its monomeric state, as in ethanol.

EXPERIMENTAL

Electronic spectra were recorded on a Pye Unicam SP 8-100 Spectrophotometer in ethanol. As spectra in water is concerned, 5% of ethanol has been added. Rf 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. The ^1H nmr spectra were obtained with Jeol GX 270 spectrometer in DMSO-d_6 solution (6%).

The following carboxylic acids and carboxamide were prepared according to literature methods: 6-methylnicotinic acid [15], 4-methylnicotinic acid [16], 6-methylpicolinic acid [17], 4-methylpicolinamide [18], 2-methylisonicotinic acid [19].

Compounds **1-7** were prepared by reacting the appropriate methylpyridine carboxylic acid (or amide) (0.15 mole) with equimolecular amounts of 3,4-diaminopyridine (**1-5**) or 2,3-diaminopyridine (**6**), or 2-amino-3-hydroxypyridine (**7**) in the presence of polyphosphoric acid (85% phosphorus pentoxide, 200 g) for 2 hours at 210°. The cooled reaction mixture was poured into water, neutralized and the precipitate filtered and slurried in dilute sodium carbonate. The bases were washed with water and crystallized.

Compounds **8-12** and **14** were prepared by refluxing the corresponding bases (0.03 mole) with a large excess of methyl iodide (10 ml) for 24 hours. For compound **13** the reaction was carried out in presence also of dimethylformamide (6 ml). The cooled mixture was filtered, the precipitate washed with ether and crystallized.

Compounds **15-17** were prepared refluxing the corresponding bases (0.03 mole) with the suitable 1-iodo-*n*-alkane (0.03 mole) in a mixture of toluene (30 ml) and dimethylformamide (6 ml) for 24 hours. After cooling the precipitates were collected, washed with ether and crystallized.

Dyes **18-22** were obtained by reacting the corresponding salts, **10-14**, (0.007 mole) with *p*-dimethylaminobenzaldehyde (0.07 mole) in presence of piperidine (0.07 mole) (for compound **22** piperidine acetate was used instead of piperidine) and absolute ethanol (50 ml) as solvent. The mixtures were refluxed for 2 hours. After cooling the precipitates were filtered, washed with ether and crystallized from ethanol.

Dye **23** was prepared by refluxing salt **11** (0.003 mole) for 2 hours in absolute ethanol (30 ml) with (3-methyl-2-benzothiazolynilydene)ethanol [20] (0.003 mole) and triethylamine (0.003 mole). The crude product was collected, washed with ethyl ether and crystallized from ethanol.

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