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Substituted xanthylocyanines. II. Pyroninocyanines

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Abstract

Symmetric and unsymmetric dyes derived from 9-methylpyronine have been obtained. Their absorption spectra exhibit an intensive long-wavelength band and a weaker short-wavelength one. The absorption maximum positions and the intensity ratio for the two bands are essentially influenced by the nature of the second end nucleus. The pyroninocyanines obtained are found to be stable long-wavelength dyes.
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Keywords: Pyroninocyanine; Michler's hydrol; NIR cyanine dyes; UV–VIS spectra

1. Introduction

Synthesis of dyes absorbing light in the near IR region (NIR dyes) represents one of the most significant challenges of present-day cyanine chemistry, especially since NIR dyes offer significant advantages, as compared to those absorbing in visible region, for solving various practical problems concerning the light energy conversion [1–4].

Xanthylocyanines have long been obtained and studied [5–7]. Though absorbing light at long wavelengths (702 nm for the carbocyanine), these dyes have been of little practical interest, in contrast to their structural analogues, benzopyrylocyanines, applied, e.g. as DNA fluorescent probes [8]. The lack of use is mainly due to the xanthylocyanine instability which, in turn, arises from a very low basicity of the xanthylium nucleus. Decomposition of xanthylocyanines proceeds via addition of nucleophiles at the position 9 of the xanthylium moiety.

It is clear that the basicity of a heterocyclic nucleus can be increased by introduction of high-electron-donor substituents such as a methoxy group. To this end, we have recently obtained a number of symmetric and unsymmetric dyes based on 3,6-dimethoxy-9-methylxanthylium [9]. The methoxy substituents have been found to have a slight effect on the absorption maxima of symmetric xanthylocyanines (cf. 707 and 702 nm for substituted and unsubstituted carbocyanines, respectively). They improve considerably photo- and thermostability and decrease base lability of the dyes. The basicity of dimethoxyxanthilium nucleus, although somewhat increasing, remains nevertheless rather low. Here we focus on the synthesis and spectral studies of xanthylocyanines containing stronger electron donors, dialkylamino groups, in the end residues and anticipate a more pronounced effect than with the dimethoxyxanthylium nucleus. The cyanines with the polymethine chromophore bound to the pyronine residue have been synthesized for the first time; in terms of conventional cyanine nomenclature, we call them *pyroninocyanines*.

2. Results and discussion

The methyl group of pyronine **1** was found to be reasonably reactive in cyanine condensations (see

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Scheme 1). Thus, compound **1** reacts with triethyl orthoformate or malonaldehyde dianile hydrochloride in acetic ahydride in the presence of triethylamine to provide dyes **2a,b**. These dyes are photostable and resistant to organic bases. Their absorption spectra exhibit two bands (see Fig. 1, Table 1). A narrow and intensive ($\varepsilon = 114{,}200$) long-wavelength band of carbocyanine **2a**, with its maximum at 780 nm, corresponds to the electronic transition along the polymethine chain. As compared to the unsubstituted xanthylocarbocyanine, it is shifted bathochromically by 78 nm. For the lengthened polymethine chain (as in dicarbocyanine **2b**), the long-wavelength band displays a vinylene shift of 114 nm becoming at the same time asymmetric and diffuse. In contrast, the short-wavelength band of dyes **2a,b** found in the absorption region of the original methylpyronine nucleus **1,** at 543 nm, is practically insensitive to the lengthening of the polymethine chromophore.

On the formal basis, it might be assumed that the closest analogues of the dyes concerned are represented by the long-known compounds **5** in which the chain is terminated by the residues of Michler's hydrol [10,11]. Dyes **5a** and **5b** also display two absorption bands each (at 636 and 810 nm, and at 663 and 910 nm, respectively), the long-wavelength band arising from the electronic transition along the polymethine chromophore and the short-wavelength one corresponding to the electronic transition within the chromophore of Michler's hydrol.

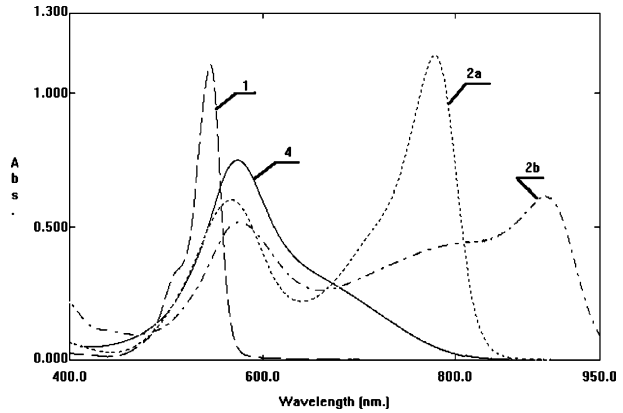
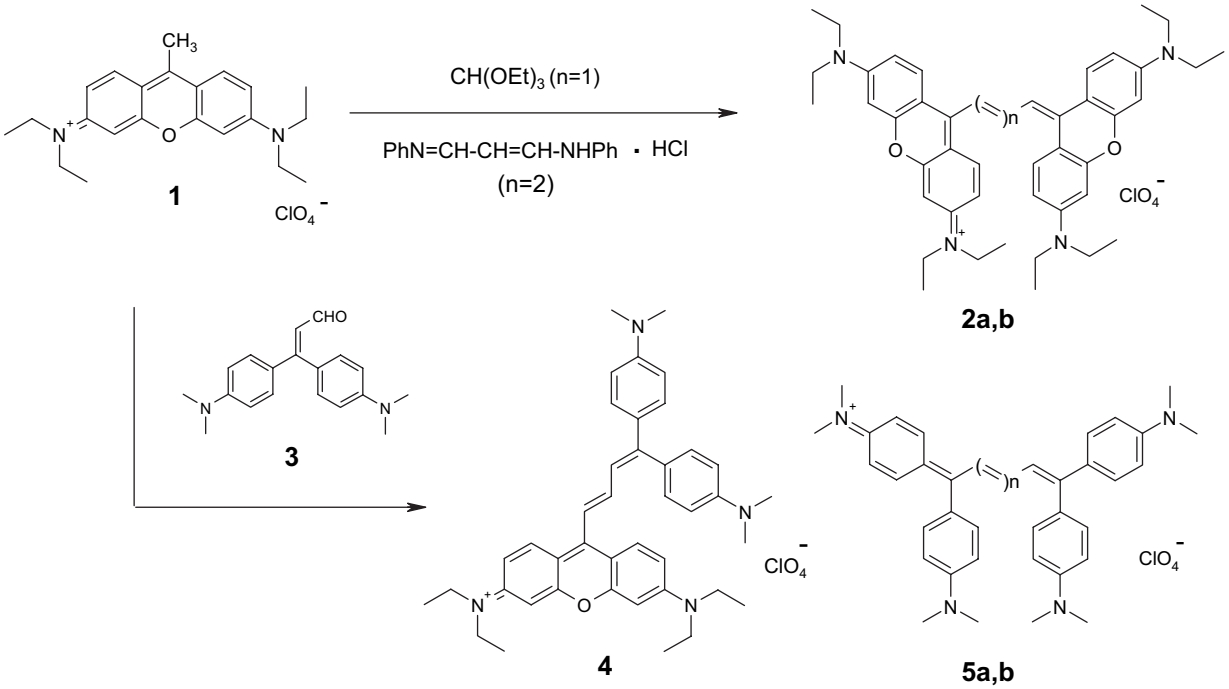


Fig. 1. Absorption spectra of dyes **1**, **2a,b** and **4** in acetonitrile ($c = 1 \times 10^{-5}$ M).

In order to ascertain whether the nuclei of pyronine and Michler's hydrol are alike as dye end groups, ''hybrid'' dye **4** was obtained. If its end groups were much the same in nature, the spectral characteristics of such a compound would be intermediate between those of **2a** and **5a**. It has turned out, however, that the absorption curve of compound **4** shows no likeness to the corresponding ''mother'' dyes and contains the only



Scheme 1.

Table 1
Characterization data for compounds **2–11**

Compound	λ_{max}, nm ($\epsilon\times10^{-4}$)	Mp (°C)	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	N		C	H	N	
2a	568 (6.03), 780 (11.42)	255–256	68.9	7.0	7.1	$C_{45}H_{55}ClN_4O_6$	68.5	6.9	7.0	61
2b	576 (5.18), 894 (6.18)	254–255	69.7	7.0	6.9	$C_{47}H_{57}ClN_4O_6$	69.6	7.2	7.0	25
3	–	174–176 (171–172 [12])	77.3	7.6	9.4	$C_{19}H_{22}N_2O$	77.5	7.5	9.5	84
4	574 (7.47)	266–267	69.0	6.9	7.8	$C_{41}H_{49}ClN_4O_5$	69.4	7.0	7.8	75
6a	561 (8.76, $CHCl_3$)	215–216	65.5	6.7	7.4	$C_{31}H_{38}ClN_3O_5$	65.0	6.5	7.3	65
7	445 (2.16), 557 (8.41)	249–251	63.9	6.2	7.2	$C_{31}H_{36}ClN_3O_6$	64.1	6.3	7.4	65
8a	548 (5.34), 651 (10.76)	247–248	67.7	6.8	6.8	$C_{35}H_{42}ClN_3O_5$	67.6	6.6	6.7	80
8b	646 (7.20)	226–227	69.6	6.5	7.7	$C_{31}H_{35}BF_4N_3$	69.4	6.6	7.8	47
9a	541 (3.96), 663 (12.19)	228–229	62.9	5.9	6.9	$C_{32}H_{36}ClN_3O_5S$	72.0	5.9	6.7	50
9b	595 (5.02)	258–259	62.9	5.6	7.7	$C_{28}H_{30}ClN_3O_4S$	62.7	5.6	7.8	66
10a	533 (2.80), 684 (12.04)	261–262	67.5	6.3	6.9	$C_{34}H_{38}ClN_3O_5$	67.2	6.3	6.8	69
10b	585 (4.51)	140–142	73.2	6.6	6.8	$C_{37}H_{39}N_3O_3S$	73.4	6.5	6.9	17
11a	569 (6.82), 671 (8.05)	248–249	68.0	7.5	4.3	$C_{37}H_{49}ClN_2O_6$	68.3	7.7	4.1	38

short-wavelength and relatively weak band ($\lambda_{max} = 574$ nm, $\varepsilon = 74{,}700$).

To obtain a deeper insight into the colour of the pyronine dyes as well as the relation between the pyronine nucleus and Michler's hydrol, it was essential to obtain a number of unsymmetric dyes (see Scheme 2).

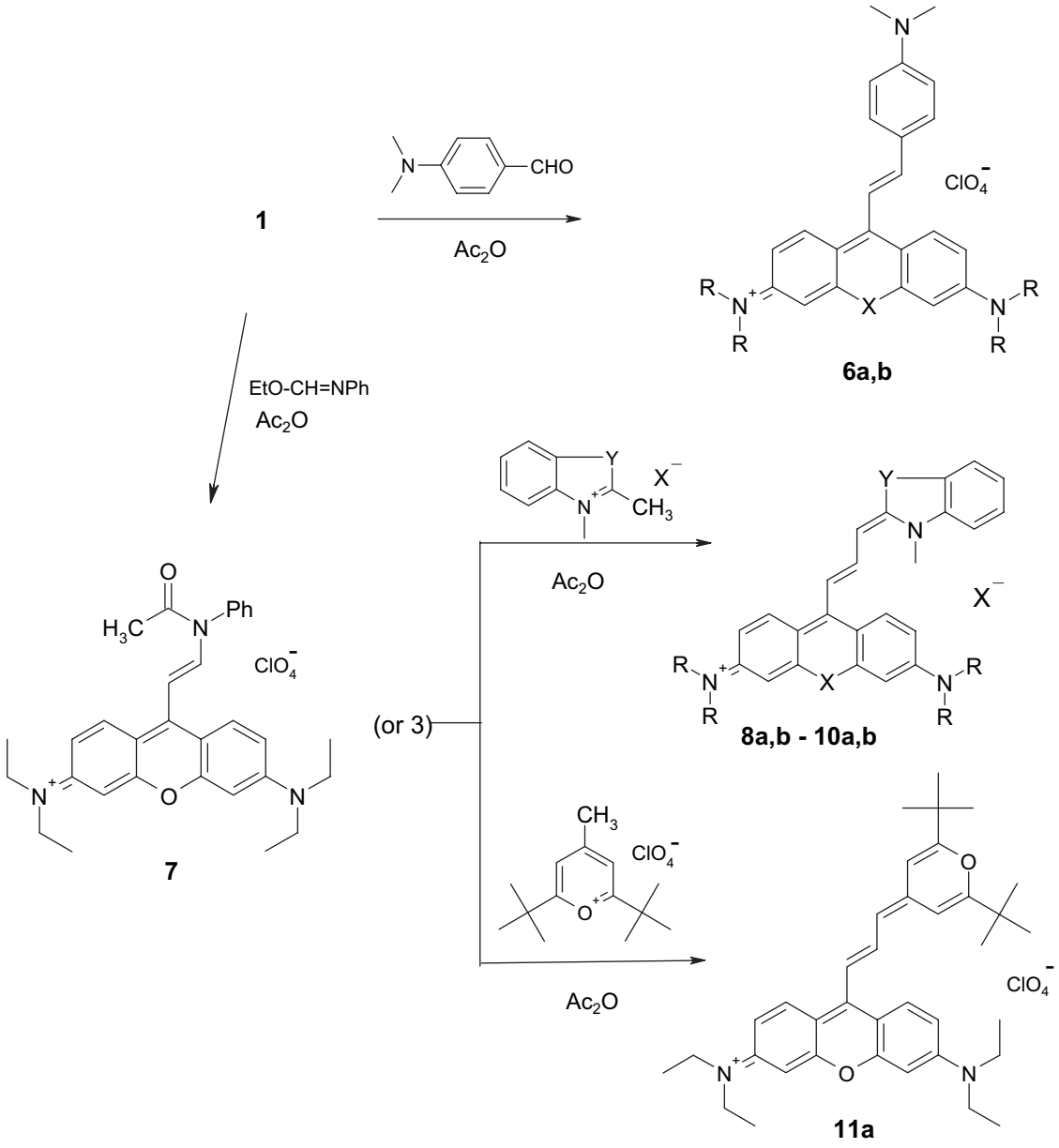
For this purpose, methylpyronine **1** was reacted with *p*-dimethylaminobenzaldehyde in acetic anhydride to furnish styryl **6a**. The reaction of methylpyronine with ethylisoformanilide led to hemicyanine **7** which reacted with the quaternary salts of 2-methylbenzothiazolium, 2,3,3-trimethylindolinium, 2-methylquinolinium, and 2,6-di-*tert*-butyl-4-methylpyrylium to yield the corresponding unsymmetric carbocyanines **8a–11a**. Their structural analogues **8b-10b** were obtained from aldehyde **3** likewise. For convenience, styryl **6b** described in the literature [11] is also presented in Scheme 2.

The absorption spectra for the family **b** dyes derived from Michler's hydrol appear to be typical of styryls: they contain a single comparatively low-intensity band slightly depending on the nature of the second end group. Thus, the residue of Michler's hydrol, if considered as a dye end nucleus, reduces to a *p*-dimethylaminophenyl group and the other *p*-dimethylaminophenyl ring is actually a substituent in the polymethine chain. As one might expect from the congested dye structure, this second ring is twisted out of the chromophore plane, which is corroborated by the non-equivalent ^{1}H NMR signals of the protons in the two *p*-dimethylaminophenyl nuclei (see the experimental part).

Introduction of an oxygen bridge into dye **b** structures, i.e. a switch to the pyroninocyanine family **a**, causes a major change in dye spectral properties. As seen from Table 1 and Fig. 2, the absorption spectrum of styryl **6a** displays the only wide band with a bend at long wavelengths. In contrast, compounds **8a–11a** are characterized by two absorption bands, long-wavelength and short-wavelength, the former being more intensive and narrower. The intensity ratio for the two bands as well as the position of the short-wavelength absorption maximum substantially depend on the electron donor ability of the second heterocyclic nucleus.

Whereas the absorption of styryl **6a** is much more intensive at short than at long wavelengths, pyrylium-containing compound **11a** is characterized by the comparable intensities of the long-wavelength and short-wavelength bands, and a further increase in electron donor ability of the second end nucleus from 1,3,3-trimethylindolium (**8a**) to benzothiazolium (**9a**) and quinolinium (**10a**) results in the increasingly predominating long-wavelength band; at the same time, the short-wavelength absorption maximum shifts hypsochromically. Another correlation is observed for the last three dyes: the bathochromic shift of the long-wavelength band is the more pronounced, the larger is the effective length of the second end nucleus The deviations of dyes **8a–10a** (10, 5, and 9 nm, respectively) suggest that the electron donor ability of the 3,6-di(diethylamino)xanthylium nucleus is much the same as that of benzothiazolium, i.e. has a medium value. As a consequence, the positive charge is mainly localized on the pyronine moiety in the molecules of dyes **6a** and **11a** containing the low-electron-donor second end group. Accordingly, a prevailing electron transition is that localized within the heterocycle. In the dye molecules bearing medium- and high-electron-donor heterocyclic nuclei, the positive charge is distributed more evenly between two end groups, so that the long-wavelength transition involving the polymethine chromophore becomes more intensive.

This inference is also supported by ^{1}H NMR spectral data. The difference in the chemical shifts between the α-CH and α′-CH protons of the polymethine chain is slight for dyes **9a** and **10a** (0.25 and 0.13 ppm, respectively) but it grows as the basicity of the second



Scheme 2.

end nucleus diminishes (0.85 ppm for the indolenine derivative **8a** and 1.04 ppm for the pyrylium derivative **11a**).

3. Experimental

Electronic absorption spectra were recorded on a spectrophotometer Shimadzu UV-3100 in acetonitrile. ^{1}H NMR spectra were recorded on a Varian VXR-300 instrument at 300 MHz. The spectral characteristics, yields, melting points, and elemental analysis data of the synthesized dyes are summarized in Table 1.

*3.1. 3,6-Di(diethylamino)-9-(3-(3,6-di(diethylamino)xanthen-9-ylidene)-1-propenyl)-xanthylium perchlorate **(2a)***

To salt **1** (0.22 g, 0.5 mmol) was added triethyl orthoformate (0.2 g, 1.5 mmol) in acetic anhydride

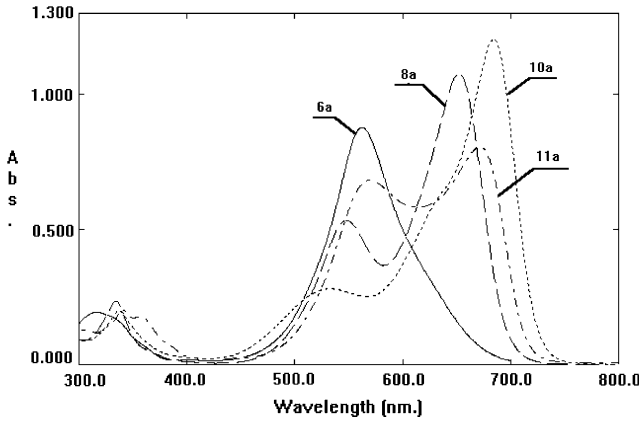


Fig. 2. Absorption spectra of dyes **6a, 8a, 10a** and **11a** in acetonitrile ($c=1\times10^{-5}$ M).

(2 ml) and the mixture was boiled for 15 min. On cooling, diethyl ether (20 ml) was added and then decanted from the resulting oily precipitate. The oil was dissolved in acetic ahydride (2 ml) and to the solution were added salt **1** (0.22 g, 0.5 mmol) and triethylamine (0.1 ml). The mixture was boiled for 10 min. The precipitate formed on cooling was filtered off and washed with acetic acid and diethyl ether. Yield 0.24 g.

^{1}H NMR (DMSO-d_6/TMS), δ: 1.17 (24H, t, CH_3); 3.52 (16H, br d, NCH_2); 6.61 (4H, s, $H_4+H_5+H'_4+H'_5$); 6.91 (4H, d, $J=9.0$ Hz, $H_2+H_7+H'_2+H'_7$); 7.34 (2H, d, $J=13.2$ Hz, α-CH + α′-CH); 7.92 (4H, d, $J=9.0$ Hz, $H_1+H_8+H'_1+H'_8$); 8.14 (1H, t, $J=13.2$ Hz, β-CH).

3.2. 3,6-Di(diethylamino)-9-(5-(3,6-di(diethylamino)xanthen-9-ylidene)-1,3-pentadienyl)-xanthylium perchlorate ***(2b)***

To salt **1** (0.44 g, 1 mmol) were added malonaldehyde dianile hydrochloride (0.13 g, 0.5 mmol) and 0.1 ml triethylamine in acetic ahydride (2 ml), and the mixture was boiled for 10 min. On cooling, diethyl ether (6 ml) was added and the mixture was allowed to stand overnight. The resulting precipitate was filtered off and washed with ethanol and diethyl ether. Yield 0.1 g.

^{1}H NMR ($CDCl_3$/TMS), δ: 1.24 (24H, t, CH_3); 3.47 (16H, br d, N-CH_2); 6.42 (4H, s, $H_4+H_5+H'_4+H'_5$); 6.7–6.8 (7H, m, $H_2+H_7+H'_2+H'_7$ + α-CH + α′-CH + γ-CH); 7.53 (2H, t, $J=13.2$ Hz, β-CH + β′-CH); 7.77 (4H, d, $J=9.3$ Hz, $H_1+H_8+H'_1+H'_8$).

3.3. 3,3-Di(4-dimethylaminophenyl)acrolein ***(3)***

To a suspension of 1,1-di(*p*-dimethylaminophenyl)-ethylene (10.0 g, 37 mmol) in DMF (30 ml) was added dropwise $POCl_3$ (3.8 ml, 41 mmol) in DMF (20 ml) so that the temperature of the mixture did not exceed 25 °C. Then the mixture was stirred at room temperature for 5 h. After adding water, the mixture was neutralized at cooling with 20% aqueous NaOH. The precipitate formed was filtered off and recrystallized from isopropanol. Yield 9.3 g.

^{1}H NMR ($CDCl_3$/TMS), δ: 3.01 (6H, s, NCH_3); 3.03 (6H, s, NCH_3); 6.42 (1H, d, $J=9.0$ Hz, CH); 6.68 (2H, d, $J=8.7$ Hz, ArH); 6.71 (2H, d, $J=9.0$ Hz, ArH); 7.21 (2H, d, $J=9.0$ Hz, ArH); 7.31 (2H, d, $J=8.7$ Hz, ArH); 9.45 (1H, d, $J=9.1$ Hz, CHO).

3.4. 3,6-Di(diethylamino)-9-(4,4-di(4-dimethylaminophenyl)-1,3-butadienyl)xanthylium perchlorate ***(4)***

To salt **1** (0.22 g, 0.5 mmol) was added 3,3-di(4-dimethylaminophenyl)acrolein **3** (0.15 g, 0.5 mmol) in acetic ahydride (3 ml) and the mixture was boiled for 2–3 min. The precipitate formed on cooling was filtered off and washed with acetic acid and diethyl ether. Yield 0.27 g.

^{1}H NMR (DMSO-d_6/TMS), δ: 1.23 (12H, t, CH_3); 2.98 (12H, d, NCH_3); 3.57 (8H, br d, NCH_2); 6.73 (4H, m, H_4+H_5 + ArH); 6.85 (2H, d, $J=8.7$ Hz, ArH); 7.1–7.3 (8H, m); 7.53 (1H, d, $J=13.8$ Hz, α-CH); 7.96 (2H, d, $J=9.6$ Hz, H_1+H_8).

3.5. 3,6-Di(diethylamino)-9-(2-(4-dimethylaminophenyl)vinyl)xanthylium perchlorate ***(6a)***

To salt **1** (0.22 g, 0.5 mmol) were added *p*-dimethylaminobenzaldehyde (0.15 g, 1 mmol), acetic ahydride (1.5 ml), and acetic acid (1.5 ml). The mixture was heated at 100 °C for 30 min. On cooling, diethyl ether (25 ml) was added and then decanted from the resulting oily precipitate. The oil was treated with hot ethanol and filtered. Yield 0.18 g.

^{1}H NMR ($CDCl_3$/TMS), δ: 1.31 (12H, t, CH_3); 3.07 (6H, s, NCH_3); 3.57 (8H, br d, NCH_2); 6.65 (2H, s, H_4+H_5); 6.72 (2H, d, $J=8.4$ Hz, ArH); 6.94 (2H, d, $J=9.2$ Hz, H_2+H_7); 7.28 (1H, d, $J=15.6$ Hz, α-CH); 7.45 (1H, d, $J=15.6$ Hz, β-CH); 7.61 (2H, d, $J=8.4$ Hz, ArH); 8.01 (2H, d, $J=9.2$ Hz, H_1+H_8).

3.6. 9-(2-Acetanilidovinyl)-3,6-di(diethylamino)xanthylium perchlorate ***(7)***

To salt **1** (0.87 g, 2 mmol) was added ethylisoformanilide (0.60 g, 4 mmol) in acetic ahydride (6 ml) and the mixture was heated at 100 °C for 20 min. On cooling, diethyl ether (20 ml) was added. The resulting precipitate was filtered off and recrystallized from ethanol. Yield 0.76 g.

^{1}H NMR (DMSO-d_6/TMS), δ: 1.21 (12H, t, CH_3); 2.02 (3H, s, $COCH_3$); 3.61 (8H, br d, NCH_2); 5.78 (1H, d, $J=14.1$ Hz, β-CH); 6.81 (2H, s, H_4+H_5); 7.15 (2H, d,

J=9.6 Hz, H_2+H_7); 7.6–7.8 (7H, m); 8.24 (1H, d, J=14.1 Hz, α-CH).

3.7. Dyes **8a–11a.** General procedure

To hemicyanine **9** (0.29 g, 0.5 mmol) was added the corresponding quaternary salt (0.5 mmol) in acetic ahydride (2 ml). The mixture was heated to boiling and triethylamine (0.1 ml) was added to it. The precipitate formed on cooling was filtered off and washed with acetic acid and diethyl ether.

3.8. 3,6-Di(diethylamino)-9-(3-(1,3,3-trimethyl-2,3-dihydroindol-2-ylidene)-1-propenyl)xanthylium perchlorate **(8a)**

^{1}H NMR (DMSO-d_6/TMS), δ: 1.29 (12H, t, CH_3); 1.62 (6H, s, CH_3); 3.55 (11H, m, NCH_2+NCH_3); 6.37 (1H, d, J=12.9 Hz, γ-CH); 6.56 (2H, s, H_4+H_5); 6.85 (2H, d, J=9.3 Hz, H_2+H_7); 6.97 (1H, d, J=7.5 Hz, H_4'); 7.1 (1H, t, J=7.5 Hz, H_5'); 7.28 (3H, m, $H_6'+H_7'$+α-CH); 7.98 (2H, d, J=9.3 Hz, H_1+H_8); 8.03 (1H, t, J=13.2 Hz, β-CH).

3.9. 3,6-Di(diethylamino)-9-(3-(3-methyl-(3H)-benzothiazol-2-ylidene)-1-propenyl)xanthylium perchlorate **(9a)**

^{1}H NMR (DMSO-d_6/TMS), δ: 1.18 (12H, t, CH_3); 3.49 (8H, NCH_2); 3.89 (3H, s, N-CH_3); 6.58 (2H, s, H_4+H_5); 6.88 (3H, m, H_2+H_7+CH); 7.09 (1H, d, J=13.2 Hz, CH); 7.44 (1H, t, J=7.5 Hz, H_5'); 7.63 (1H, t, J=7.5 Hz, H_6'); 7.7–8.02 (5H, m).

3.10. 3,6-Di(diethylamino)-9-(3-(1-methyl-(1H)-quinolin-2-ylidene)-1-propenyl)xanthylium perchlorate **(10a)**

^{1}H NMR (DMSO-d_6/TMS), δ: 1.17 (12H, t, CH_3); 3.51 (8H, br d, NCH_2); 4.12 (3H, s, NCH_3); 6.52 (2H, s, H_4+H_8); 6.82 (2H, d J=9.3 Hz, H_2+H_7); 7.00 (1H, d, J=12.9 Hz, CH); 7.13 (1H, d, J=12.3 Hz, CH); 7.61 (1H, t, H_6'); 7.89 (3H, m, $H_2+H_7+H_7'$); 7.99 (1H, d, J=7.8 Hz, H_8'); 8.1 (1H, d, J=9.3 Hz, H_3'); 8.16 (1H, d, J=9.3 Hz, H_5'); 8.27 (1H, d J=9.3 Hz, H_4'); 8.4 (1H, t, J=12.9 Hz, β-CH).

3.11. 3,6-Di(diethylamino)-9-(3-(2,6-di-tert-butyl)-pyran-4-ylidene)-1-propenyl)xanthylium perchlorate **(11a)**

^{1}H NMR (DMSO-d_6/TMS), δ: 1.25 (30H, m); 3.58 (8H, br d, NCH_2); 6.18 (1H, d, J=12.6 Hz, γ-CH); 6.32 (1H, s, H_3'); 6.75 (3H, d, $H_4+H_5+H_5'$); 7.05 (2H, d, J=9.6 Hz, H_2+H_7); 7.22 (1H, d, J=13.8 Hz, α-CH); 8.02 (3H, m, H_1+H_8+β-CH).

3.12. Dyes **8b–10b.** General procedure

Aldehyde **3** (0.29 g, 1 mmol) and the corresponding quaternary salt (1 mmol) in acetic ahydride (3 ml) were boiled for 5 min. On cooling, diethyl ether (20 ml) was added and decanted, and the residue was recrystallized.

3.13. 2-(4,4-Di(4-dimethylaminophenyl)-1,3-butadien-1-yl)-1,3,3-trimethyl-2,3-dihydroindolium tetrafluoroborate **(8b)**

The product was recrystallized from EtOH. Yield 0.25 g.

^{1}H NMR (DMSO-d_6/TMS), δ: 1.47 (6H, s, $C(CH_3)_2$); 3.07 (12H, s, NCH_3); 3.84 (3H, s, NCH_3); 6.81 (2H, d J=8.7 Hz, ArH); 6.88 (2H, d, J=8.4 Hz, ArH); 7.05 (1H, d, J=14.7 Hz, γ-CH); 7.16–7.25 (3H, m, ArH+α-CH); 7.38–7.46 (3H, m, ArH+H_7); 7.53 (1H, t, J=7.5 Hz, H_5); 7.67 (2H, t, H_4+H_6); 7.81 (1H, t, β-CH).

3.14. 2-(4,4-Di(4-dimethylaminophenyl)-1,3-butadien-1-yl)-3-methylbenzothiazolium perchlorate **(9b)**

The product was recrystallized from EtOH. Yield 0.35 g.

^{1}H NMR (DMSO-d_6/TMS), δ: 3.02 (12H, s, NCH_3); 4.12 (3H, s, NCH_3); 6.76 (2H, d, J=8.1 Hz, ArH); 6.86 (2H, d, J=8.7 Hz, ArH); 7.14 (3H, m, ArH+CH); 7.31 (2H, d, J=8.7 Hz, ArH); 7.4–7.8 (3H, m, 2CH+H_5); 7.75 (1H, t, H_6); 8.05 (1H, d J=8.4 Hz, H_7); 8.18 (1H, d, J=7.5 Hz, H_4).

3.15. 2-(4,4-Di(4-dimethylaminophenyl)-1-methyl-1,3-butadien-1-yl)quinolinium tosylate **(10b)**

The product was recrystallized from i-PrOH. Yield 0.1 g.

^{1}H NMR (DMSO-d_6/TMS), δ: 2.23 (3H, s, CH_3); 3.02 (12H, d, NCH_3); 4.38 (3H, s, NCH_3); 6.76 (2H, d, J=9.2 Hz, ArH); 6.86 (2H, d, J=8.4 Hz, ArH); 7.09–7.18 (5H, m, ArH+CH); 7.28 (2H, d, J=9.2 Hz, ArH); 7.42–7.52 (3H, m, ArH+CH); 7.69–7.85 (2H, m, H_7+CH); 8.0–8.1 (2H, m, H_6+H_3); 8.21 (1H, d, J=7.8 Hz, H_5); 8.38 (1H, d, J=9.3 Hz, H_8); 8.66 (1H, d, J=9.3 Hz, H_4).

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