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Substituted xanthylocyanines. III. Dyes containing non-symmetrically substituted xanthylium core

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Abstract

A series of symmetrically and non-symmetrically substituted dyes were prepared from 9-methylxanthylium salts. The absorbance spectra of these compounds contain two bands – intense longwave and less intense shortwave. The nature of electronic transitions in polymethine dyes and dependence of the position and intensity of absorbance bands on the structure of end nucleus are discussed. The electron-donating properties of the synthesized xanthylium cores were studied.

Keywords: Xanthylium dyes; NIR cyanine dyes; UV–vis spectra; NMR spectra

1. Introduction

We have recently synthesized a series of substituted xanthylocyanines [1,2] that, in contrast to previously described non-substituted analogues [3–5], appeared to be photo- and thermostable longwave dyes. This was achieved by the incorporation of two electron-donating substituents at positions 3 and 6 of the end nucleus, namely methoxy [1] and diethylamino [2] groups. Absorbance spectra of the dyes contain two bands, their position and intensity depend strongly on the nature of the second end nucleus. The substitution effect was considerably higher for 3,6-bis(diethylamino)xanthylium dyes. One could therefore suppose that there is an interaction between chromophores as a factor influencing the spectral properties of these dyes based on deeply coloured nuclei.

From this point of view, it would be possible to decrease the effect of chromophores interaction and therefore achieve the deeper colour of corresponding dyes. So the goal of the present work was the preparation and spectral studies of xanthylocyanines containing single dialkylamino group in xanthylium nucleus.

2. Results and discussion

To achieve the above goal, methods of preparation of the salts **9a** and **9b**, key intermediates for the target dyes synthesis, have been developed. Starting compound for their synthesis was acetophenone **3**. The synthesis of 2-hydroxy-4-dimethylaminoacetophenone **3a** by Fries rearrangement of acetoxydimethylaniline **1** was previously reported ([6], yield: 15%). This method, however, is not technically convenient, so we have developed another synthetic approach. We have found that the treatment of 7-diethylamino-4-hydroxycoumarine **2** available on preparative scale [7] with mineral acids led to the high yield formation of acetophenone **3b** via the ring opening with decarboxylation. More advantageous reaction conditions have also been found for the preparation of compound **5** – the coupling is better to be performed in phosphoric acid instead of sulphuric acid that was proposed before for compound **4** [6] (Scheme 1).

Rhodol **5** can be isolated as a free base or in more convenient form of salt **6**. We were not able to alkylate compound **5** in the absence of the bases, whereas addition of the base resulted in

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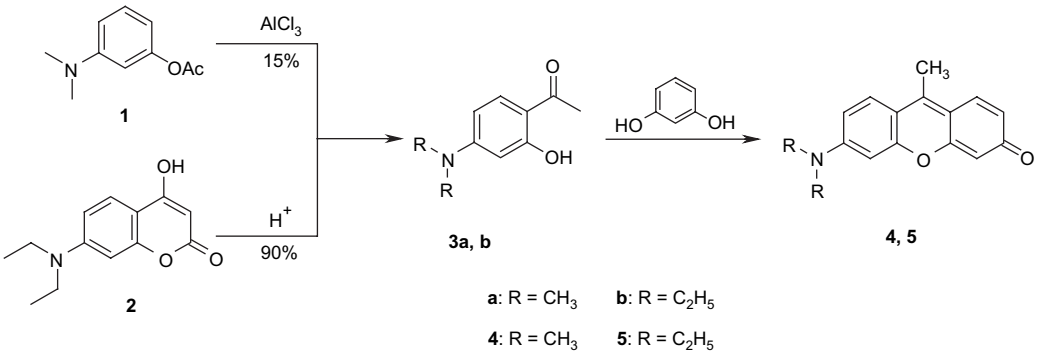


Scheme 1.

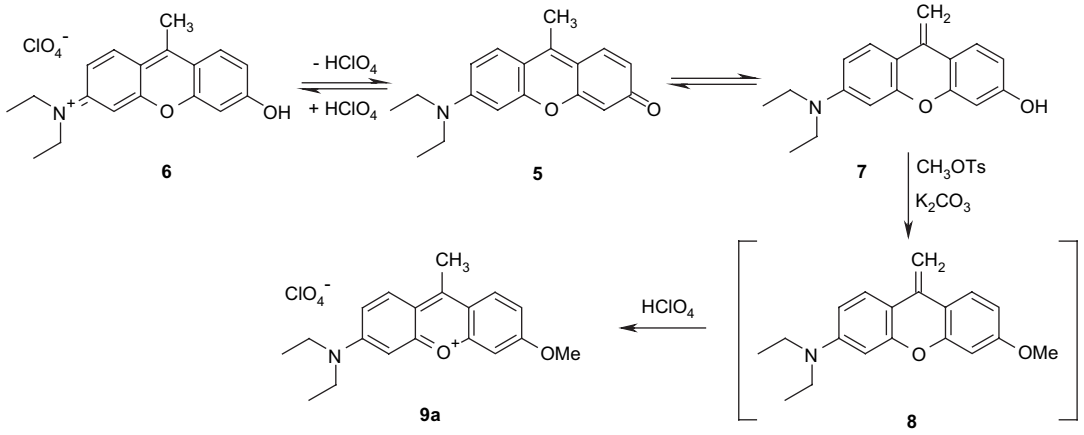
smooth alkylation. Possible intermediate of this reaction can be methylene base **7** that would explain why the base is necessary. The product of methylation **8** was isolated, although not characterised, and formed salt **9a** upon acidification (Scheme 2).

To obtain monosubstituted xanthylium salt **9b**, acetophenone **10** prepared by the alkylation of compound **3b** was reacted with 2-anisylmagnesiumbromide. The heating of the obtained alcohol **11** in the mixture of hydrobromic and acetic acids resulted in one-step demethylation and cyclization. Perchlorate salt **9b** was isolated (Scheme 3).

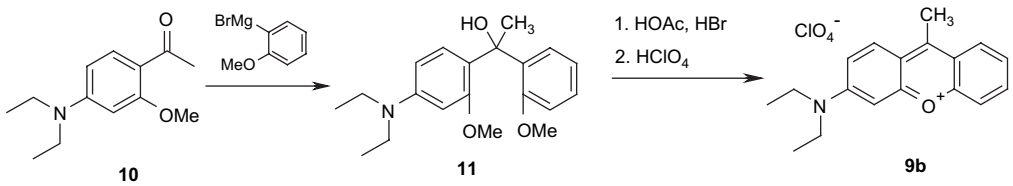
9-Methyl group of the starting salts is sufficiently reactive to form polymethine dyes. Symmetric carbocyanines **12a**,**b** were obtained upon interaction of xanthylium salts **9a**,**b** with triethyl orthoformate in pyridine. Reaction of the salts **9a**,**b** with 4-dimethylaminobenzaldehyde and formylmethyl derivatives of 1,3,3-trimethylindolenine, *N*-methylbenzothiazole and 2,6-diphenylpyrane in acetic anhydride led to the formation of styryls **13a**,**b** and non-symmetric trimethinecyanines **14a**,**b**, **15a**,**b** and **17a**,**b**, whereas dyes **16a**,**b** were obtained with 1-methyl-2-(2-phenylaminovinyl)quinolinium tosylate (Scheme 4).

Two absorption peaks, longwave band of the chromophore localized along polymethine chain, and shortwave band of xanthene nucleus, are observed in the absorbance spectra of symmetric dyes, as well as corresponding pyroninocyanines [2]. When comparing spectra of symmetric trimethinecyanines from five series of xanthylium dyes (non-substituted (type A)) [3–5], 3,6-dimethoxy- (B) [1], 3,6-bis(diethylamino)- (C) [2], 3-methoxy-6-diethylamino- (D, **12a**) and 3-diethylamino- (E, **12b**) derivatives (Table 1, Fig. 1) some regularities can be found. Bathochromic shift of the longwave absorbance band is observed upon the transition from type A to type E dyes. It should be taken into account that several factors affect the colour of symmetric trimethinecyanines. First, the substitution of xanthylium nucleus with electron-donating groups increasing the efficiency of positive charge delocalisation generally promotes the red shift. Second, relatively long wavelength electron transition localized in xanthene nucleus makes possible its interaction with transition localized at polymethine chain. Such an interaction effects on the spectral position of the dyes absorbance bands. For example, in the case of pyroninocyanine (type C) the difference between short- and longwave maxima is 4785 cm^{-1}. After the substitution of one diethylamino group for methoxy residue (D, **12a**) the difference increases to 5839 cm^{-1}, and upon diethylamino group substitution for hydrogen atom (E, **12b**) the difference is 5994 cm^{-1}. For the type B dye, the energy of shortwave transition exceeds considerably the transition energy for the nucleus containing diethylamino substituent, and the corresponding difference reaches 8532 cm^{-1}.

Thus, upon the substitution of strong electron donor diethylamino group for methoxy group (**12a**), hydrogen (**12b**), and then changing both diethylamino residues for methoxy groups,



Scheme 2.



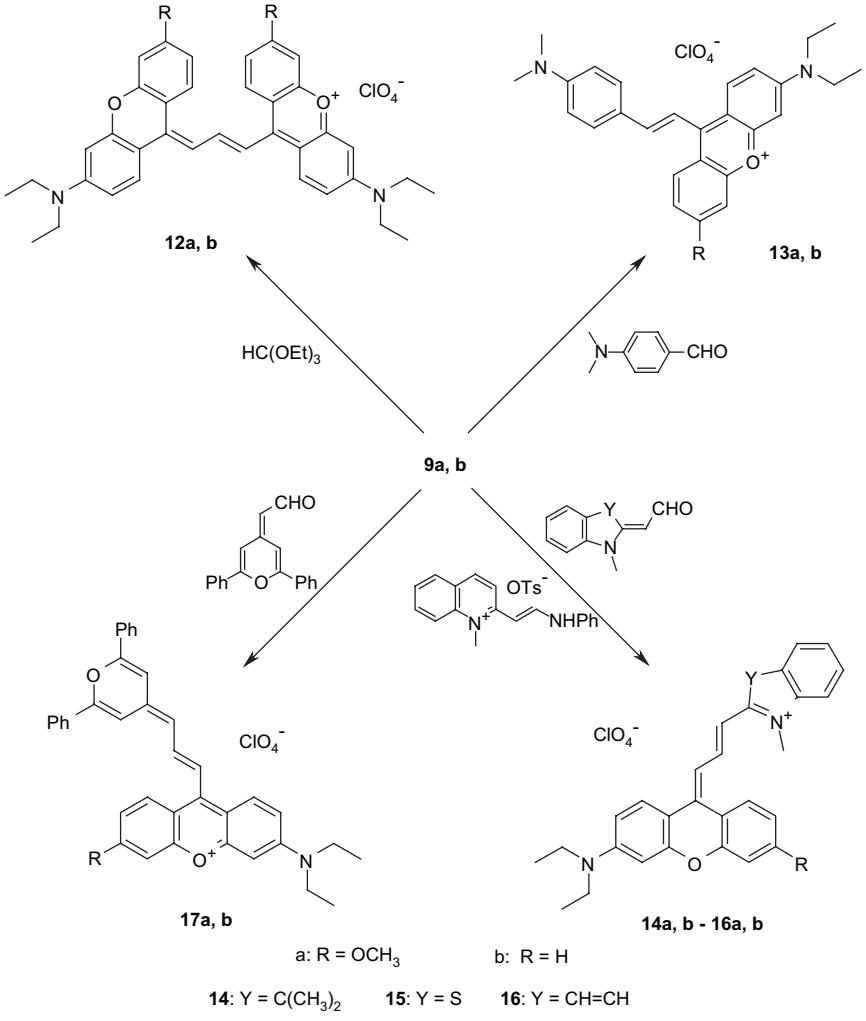
Scheme 3.

the shortwave transition energy gradually increases that results in the increasing distance between short- and longwave absorbance bands of the dyes. In its turn, this weakens the interaction of nuclear and polymethine chromophores.

The introduction of asymmetry elements into the xanthylium nucleus somewhat complicates electronic spectra of the respective dyes due to the possibility of three stereoisomers (Scheme 5).

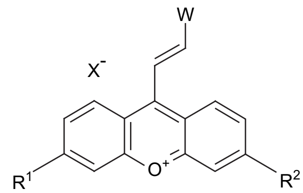
The decrease in absorbance intensities and broadening of longwave bands (half-width of corresponding bands is 1295 cm^{-1} for C series, 1707 cm^{-1} for D (**12a**) and 2015 cm^{-1} for E (**12b**) may indicate the presence of stereoisomers (Fig. 1).

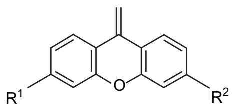
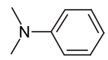
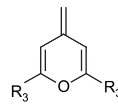
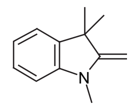
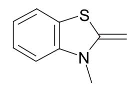
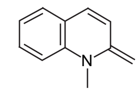
The absorbance spectra of styryls **13a**,**b** also contain two bands (Table 1). The positions of shortwave absorption bands of styryls almost coincide with those of the respective xanthene nuclei. With decreasing basicity of xanthene nucleus, bathochromic shift of the longwave band is observed, along with the increase in transition intensity (Fig. 2). For the styryl containing the most basic pyronine nucleus (type C) the spectrum appears as a single broad band with a slight longwave curve bend. Two bands of close intensities are observed for styryl **13a** (type D). There is a red shift of the longwave band in the case of **13b** (for 35 nm as comparing to **13a**), the intensity of nucleus transition being twice lower. The spectrum of styryl B consists of intense



Scheme 4.

Table 1
Spectral characteristics of synthesized compounds in acetonitrile



Type	R^1, R^2	W										
												
		λ_{max} (nm) ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$)	λ_{max} (nm) ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$)	$\Delta\lambda$	λ_{max} (nm) ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$)	$\Delta\lambda$	λ_{max} (nm) ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$)	$\Delta\lambda$	λ_{max} (nm) ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$)	$\Delta\lambda$	λ_{max} (nm) ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$)	$\Delta\lambda$
A	H, H; [3–5]	704 (69)										
B	OCH_3, OCH_3;	441 (30)	428 (25)		410 (26)		384 (10)		541 (46)	90.0	–	–
	[1]	707 (89)	670 (70)	−14	684 (96), (R_3 = Ph)	7.5	573 (50)	51.5				
C	$N(Et)_2$, $N(Et)_2$;	568 (60)	561 (88)	131.5	569 (68)		548 (53)		541 (40)		533 (28)	
	[2]	780 (114)	($CHCl_3$)		671 (80), (R_3 = *t*-Bu)		651 (108)	10.0	663 (122)	4.5	684 (120)	5.5
D	$N(Et)_2$, OCH_3	535 (26) (**12a**)	511 (45) (**13a**)		529 (26) (**17a**)		486 (22) (**14a**)		470 (17) (**15a**)		451 (12) (**16a**)	
		778 (73)	628 (46)	63.5	729 (104), (R_3 = Ph)	−2.0	663 (99)	−3.0	654 (51)	12.5	607 (48)	81.5
E	$N(Et)_2$, H	543 (18) (**12b**)	509 (24) (**13b**)		520 (16) (**17b**)		467 (14) (**14b**)		443 (11) (**15b**)		425 (11) (**16b**)	
		805 (58)	663 (45)	42.0	747 (103), (R_3 = Ph)	−6.5	673 (73)	0.5	630 (38)	50	604 (48)	98.0

$\Delta\lambda$ – Deviation.

longwave band at 670 nm and relatively weak nucleus absorption band.

The presence of stereoisomers illustrated in Scheme 5 is clearly evident also for corresponding styryls. For example, the doubling of the proton signals is observed in ^{1}H NMR spectrum of compound **13a** that directly indicates the presence of two isomers in the approximate ratio 35:65 (Fig. 3).

The above-mentioned tendencies generally come true for another non-symmetric dyes as well. Two absorbance bands are observed in electronic spectra of the dyes **14a**,**b**–**17a**,**b**.

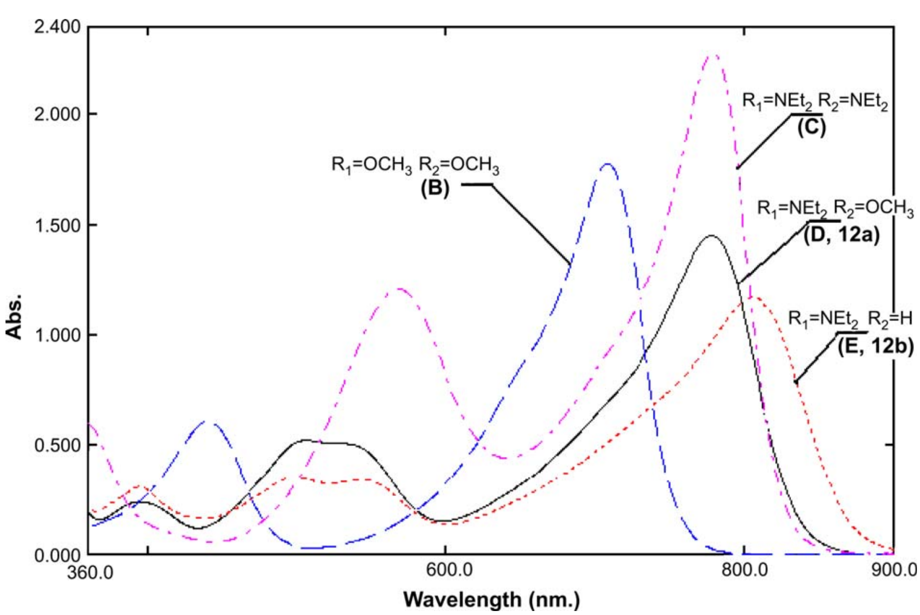
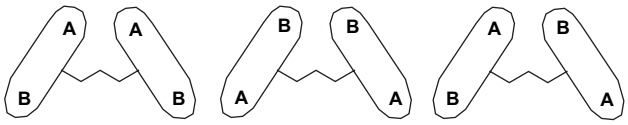


Fig. 1. Absorption spectra of **12a**,**b** and B, C [1,2] type symmetric dyes in acetonitrile (2×10^{-5} M).



Scheme 5.

Bathochromic shifts of both bands are observed upon the transition from high- to low-basic end nuclei (Table 1), and the shape and intensity of the bands change from broad low-intense for high- and medium-basic nuclei to narrow and intense bands for low-basic ones.

Due to a number of above discussed factors, first of all the presence of stereoisomers, electron-donating properties of non-symmetrically substituted xanthylium nuclei cannot be determined by deviations method (Table 1). However, as chemical shifts of polymethine chain protons in ^{1}H NMR spectra can characterise the electronic density distribution in the molecule, we have found a linear correlation between the values of chemical shifts of γ-protons (β-protons for styryls) of the chain and electron-donating level of the end nucleus by Ilchenko scale [8] within the series of uniformly substituted xanthylium dyes. According to this scale, electron donor ability of benzothiazole is 1.5 and that of indolenine is 1.0. The values for the type B and C nuclei were found by method in Ref. [8] to be −0.43 and 1.47, respectively. Electron donor abilities of the nuclei of type D and E were determined by interpolation from the series of symmetric and non-symmetric benzothiazole-based trimethinecyanines and styryls. The values found by this approach were 1.25 for the nucleus of type D (**a**) and 0.8 for type E (**b**) nucleus (Fig. 4).

Thus, transition from pyroninocyanines to the dyes containing xanthylium nucleus with a single diethylamino group results in some bathochromic shift of longwave absorbance. However, due to the factor of asymmetry the shapes of the dye absorbance bands become more complicated, along with the intensity decrease.

3. Experimental

Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in acetonitrile. Proton NMR spectra were obtained with a Varian VXR-300 instrument at 300 MHz using tetramethylsilane as an internal standard; chemical shifts are given in ppm. The spectral characteristics of the synthesized dyes are summarized in Table 1.

*3.1. 1-(4-Diethylamino-2-hydroxyphenyl)ethanone (**3b**)*

The solution of compound **2** (40 g, 0.172 mol) in 340 ml of 30% sulphuric acid was heated at 125 °C for 5 h. After cooling, the reaction mass was neutralized with aqueous ammonia, and the product was extracted with dichloromethane. The extract was dried with magnesium sulphate, and the solvent was removed. The obtained solid was recrystallized from hexane. Yield: 32 g (90%). M.p. = 42–44 °C.

^{1}H NMR ($CDCl_3$), δ: 1.20 (6H, t, J = 6.9 Hz, CH_3), 2.47 (3H, s, CH_3CO), 3.39 (4H, q, J = 6.6 Hz, NCH_2), 6.07 (1H, s, H^3), 6.18 (1H, d, J = 9.3 Hz, H^5), 7.51 (1H, d, J = 9.3 Hz, H^6). Anal. ($C_{12}H_{17}NO_2$) calcd.: C, 69.5; H, 8.3; N, 6.8; found: C, 69.3; H, 8.3; N, 6.9.

*3.2. 3-Diethylamino-6-hydroxy-9-methylxanthylium perchlorate (**6**)*

The solution of **3b** (5 g, 0.024 mol) and resorcinol (3 g, 0.027 mol) in 85% phosphoric acid (30 ml) was heated at 140 °C for 6 h. After cooling, 100 ml of water was added. The solution of $NaClO_4$ (5.2 g) in water (15 ml) was added.

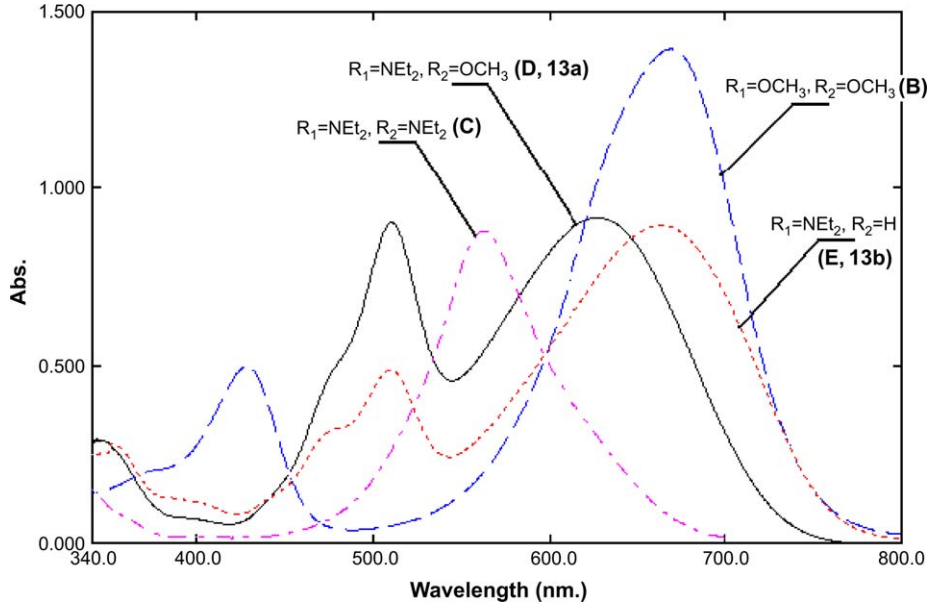


Fig. 2. Absorption spectra of **13a**,**b** and B, C [1,2] type styryl dyes in acetonitrile (2×10^{-5} M).

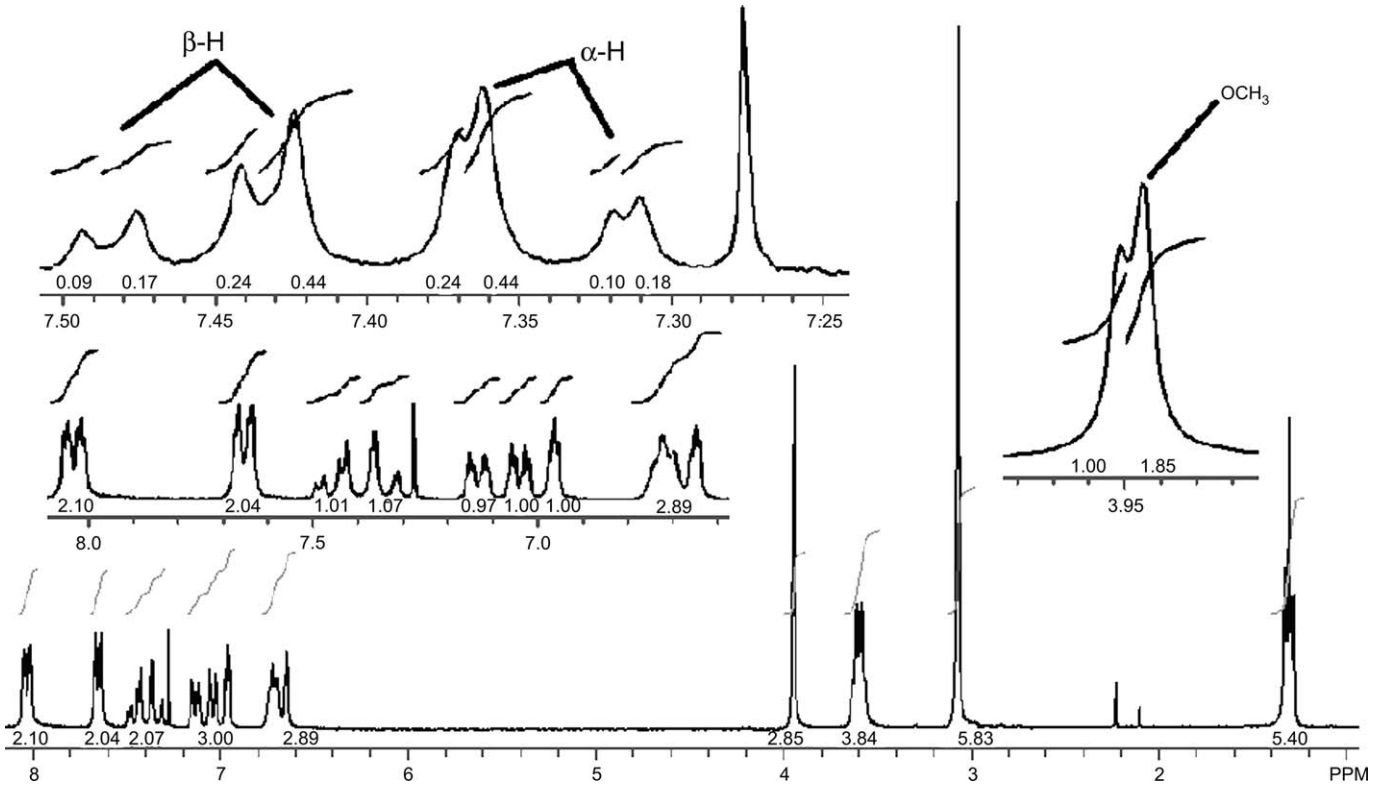


Fig. 3. ^{1}H NMR spectrum of **13a** in $CDCl_3$.

The resulting precipitate was filtered off and recrystallized from ethanol. Yield: 8.65 g (94%). M.p. = 243 °C.

^{1}H NMR (CD_3CN), δ: 1.31 (6H, t, CH_3CH_2), 2.90 (3H, s, 9-CH_3), 3.70 (4H, br s, NCH_2), 6.81 (1H, s, H^4), 7.00 (1H, s, H^5), 7.11 (1H, d, $J = 9.0$ Hz, H^2), 7.26 (1H, d, $J = 9.9$ Hz, H^7), 8.09 (1H, d, $J = 9.3$ Hz, H^1), 8.10 (1H, d, $J = 10.2$ Hz, H^8). Anal. ($C_{18}H_{20}ClNO_6$) calcd.: C, 56.6; H, 5.3; N, 3.7; Cl, 9.3; found: C, 56.5; H, 5.4; N, 3.7; Cl, 9.2.

*3.3. 6-Diethylamino-9-methylxanthen-3-one (**5**)*

To the solution of **6** (0.38 g, 1 mmol) in ethanol (15 ml), aqueous $NaHCO_3$ was added. The resulting precipitate was filtered off and washed with water. Yield: 0.21 g (75%). M.p. = 181 °C.

^{1}H NMR ($CDCl_3$), δ: 1.28 (6H, t, CH_3CH_2), 2.63 (3H, s, 9-CH_3), 3.48 (4H, q, CH_3CH_2), 6.38 (1H, s, H^5), 6.51 (1H, s, H^4), 6.69 (2H, d, $J = 9.6$ Hz, $H^2 + H^7$), 7.61 (2H, d, $J = 9.6$ Hz, $H^1 + H^8$). Anal. ($C_{18}H_{19}NO_2$) calcd.: C, 76.8; H, 6.8; N, 5.0; found: C, 77.2; H, 6.9; N, 5.0.

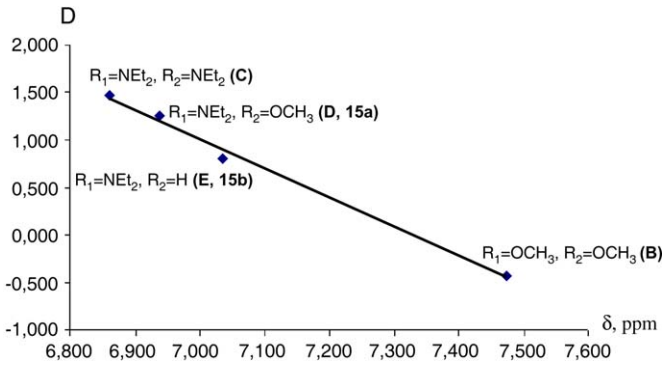


Fig. 4. Correlation between electron donor abilities (*D*) of xanthylium nuclei and chemical shifts of γ-H atom of polymethine chain in the series of thiatrimethinecyanines B, C, D (**15a**), E (**15b**).

*3.4. 3-Diethylamino-6-methoxy-9-methylxanthylium perchlorate (**9a**)*

The mixture of **6** (12 g, 0.031 mol), toluene-4-sulphonic acid methyl ester (14.7 g, 0.079 mol), K_2CO_3 (25.5 g, 0.185 mol) and 18-crown-6 (30 mg) in acetonitrile (40 ml) was refluxed for 2 h. After cooling the reaction mixture was filtered and the solvent was evaporated. The residue was dissolved in isopropanol (25 ml) and aqueous $HClO_4$ solution (57%, 11 ml) was added. The resulting precipitate was filtered off and recrystallized from acetic acid. Yield: 10.7 g (86%). M.p. = 249–250 °C.

^{1}H NMR (CD_3CN), δ: 1.31 (6H, t, $J = 7$ Hz, CH_3), 2.95 (3H, s, 9-CH_3), 3.71 (4H, q, $J = 7$ Hz, NCH_2), 4.02 (3H, s, OCH_3), 6.85 (1H, s, H^4), 7.15 (1H, s, H^5), 7.19 (1H, d, $J = 9.6$ Hz, H^2), 7.29 (1H, d, $J = 9.9$ Hz, H^7), 8.13 (1H, d, $J = 9.3$ Hz, H^1), 8.14 (1H, d, $J = 9.3$ Hz, H^8). Anal. ($C_{19}H_{22}ClNO_6$) calcd.: C, 57.7; H, 5.6; N, 3.5; Cl, 9.8; found: C, 58.0; H, 5.6; N, 3.5; Cl, 9.9. $\lambda_{max} = 509$ nm, $\varepsilon = 21\,000$ l mol^{-1} cm^{-1} (acetonitrile).

3.5. 1-(4-Diethylamino-2-methoxyphenyl)ethanone (**10**)

The mixture of **3b** (2.07 g, 0.01 mol), toluene-4-sulphonic acid methyl ester (2.05 g, 0.011 mol), K_2CO_3 (4.14 g, 0.03 mol) and 18-crown-6 (10 mg) in acetonitrile (40 ml) was refluxed for 10 h. The solution was cooled and filtered. The solvent was evaporated and the residue was recrystallized from hexane. Yield: 1.9 g (86%). M.p. = 70 °C.

^{1}H NMR ($CDCl_3$), δ: 1.23 (6H, t, CH_3CH_2), 2.56 (3H, s, CH_3CO), 3.42 (4H, q, NCH_2), 3.91 (3H, s, OCH_3), 6.09 (1H, s, H^3), 6.28 (1H, d, $J = 9$ Hz, H^5), 7.83 (1H, d, $J = 9$ Hz, H^6). Anal. ($C_{13}H_{19}NO_2$) calcd.: C, 70.6; H, 8.7; N, 6.3; found: C, 70.6; H, 8.6; N, 6.3.

3.6. 1-(2-Methoxy-4-diethylaminophenyl)-1-(2′-methoxyphenyl)ethanol (**11**)

Dry diethyl ether (40 ml) and then 2-bromoanisole (2.8 g, 0.015 mol) were added to the flask with magnesium (0.4 g, 0.017 mol, activated with a crystal of iodine), and the reaction mixture was refluxed for 3 h with stirring. Obtained Grignard reagent solution was added dropwise to the solution of **10** (2.2 g, 0.01 mol) in dry diethyl ether (40 ml) with stirring. After addition, stirring was continued for 10 min. The solution of NH_4Cl (2 g) in water (20 ml) was added. Organic layer was separated and dried with $MgSO_4$. Solvent was evaporated, and the residue was recrystallized from hexane. Yield: 1.9 g (58%). M.p. = 76–78 °C.

^{1}H NMR ($CDCl_3$), δ: 1.14 (6H, t, $J = 7.2$ Hz, CH_2CH_3), 1.90 (3H, s, CH_3COH), 3.32 (4H, q, $J = 7.2$ Hz, NCH_2), 3.49 (3H, s, OCH_3^2), 3.57 (3H, s, $OCH_3^{'2}$), 4.79 (1H, s, OH), 6.13 (1H, s, H^3), 6.29 (1H, d, $J = 8.7$ Hz, H^5), 6.79 (1H, d, $J = 8.1$ Hz, H'^3), 6.95 (1H, t, $J = 7.5$ Hz, H'^5), 7.17 (1H, t, $J = 8.4$ Hz, H'^4), 7.35 (1H, d, $J = 8.7$, H^6), 7.59 (1H, d, $J = 9.3$ Hz, H'^6). Anal. ($C_{20}H_{27}NO_3$) calcd.: C, 72.9; H, 8.3; N, 4.3; found: C, 73.2; H, 8.3; N, 4.3.

3.7. 3-Diethylamino-9-methylxanthylium perchlorate (**9b**)

The mixture of **3** (0.329 g, 1 mmol) and aqueous HBr (46%, 0.8 g, 4.5 mmol) in acetic acid (4 ml) was heated at 130 °C for 8 h. After cooling the mixture was diluted with acetic acid (5 ml), and aqueous perchloric acid (57%, 0.4 ml) was added. The resulting precipitate was filtered off and recrystallized from ethanol. Yield: 0.2 g (55%). M.p. = 204 °C.

^{1}H NMR (CD_3CN), δ: 1.33 (6H, t, CH_3), 3.0 (3H, s, 9-CH_3), 3.76 (4H, br d, NCH_2), 6.91 (1H, s, H^4), 7.39 (1H, d, $J = 9.9$ Hz, H^2), 7.63 (1H, t, $J = 7.2$ Hz, H^7), 7.71 (1H, d, $J = 8.4$ Hz, H^5), 7.97 (1H, t, $J = 7.2$ Hz, H^6), 8.16–8.28 (2H, m, $H^1 + H^8$). Anal. ($C_{18}H_{20}ClNO_5$) calcd.: C, 59.1; H, 5.5; N, 3.8; Cl, 9.7; found: C, 58.9; H, 5.6; N, 3.9; Cl, 9.7. $\lambda_{max} = 509$ nm, $\varepsilon = 16\,000$ l mol^{-1} cm^{-1} (acetonitrile).

3.8. Dyes **12a**,**b**. General procedure

The mixture of **9a**,**b** (1 mmol) and triethyl orthoformate (3 mmol) in pyridine (1.5 ml) was briefly heated to intense boiling. After cooling, diethyl ether (40 ml) was added and then decanted from the resulting oily precipitate. The latter was recrystallized from acetic acid.

3.9. 3-Diethylamino-9-[3-(3-diethylamino-6-methoxyxanthen-9-ylidene)propenyl]-6-methoxyxanthylium perchlorate (**12a**)

Yield: 40%. M.p. = 178 °C.

^{1}H NMR ($CDCl_3$), δ: 1.22 (12H, t, $J = 7.5$ Hz, CH_3), 3.45 (8H, q, $J = 7.2$ Hz, NCH_2), 3.86 (6H, s, OCH_3), 6.3 (2H, s, $H^4 + H'^4$), 6.65 (2H, s, $H^5 + H'^5$), 6.82 (2H, d, $J = 10$ Hz, $H^2 + H'^2$), 6.83 (2H, d, $J = 10$ Hz, $H^7 + H'^7$), 7.05 (2H, d, $J = 12.6$ Hz, α-H + α′-H), 7.71 (2H, d, $J = 9.3$ Hz, $H^1 + H'^1$), 7.73 (2H, d, $J = 9.3$ Hz, $H^8 + H'^8$), 7.82 (1H, t, $J = 12.9$ Hz, β-H). Anal. ($C_{39}H_{41}ClN_2O_8$) calcd.: C, 66.8; H, 5.9; N, 4.0; Cl, 5.1; found: C, 66.9; H, 6.0; N, 4.0; Cl, 5.0.

3.10. 3-Diethylamino-9-[3-(3-diethylaminoxanthen-9-ylidene)propenyl]xanthylium perchlorate (**12b**)

Yield: 34%. M.p. = 213 °C.

^{1}H NMR (DMSO-d_6), δ: 1.24 (12H, t, CH_3), 3.62 (8H, br d, NCH_2), 6.79 (2H, s, $H^4 + H'^4$), 7.13 (2H, d, $J = 9.6$ Hz, $H^2 + H'^2$), 7.48–7.62 (4H, m, $H^5 + H'^5 + H^7 + H'^7$), 7.67 (2H, d, $J = 13.2$ Hz, α-H + α′-H), 7.79 (2H, t, $J = 7.8$ Hz, $H^6 + H'^6$), 8.05 (2H, d, $J = 9.6$ Hz, $H^1 + H'^1$), 8.15 (1H, t, $J = 13.2$ Hz, β-H), 8.23 (2H, d, $J = 8.4$ Hz, $H^8 + H'^8$). Anal. ($C_{37}H_{37}ClN_2O_6$) calcd.: C, 69.3; H, 5.8; N, 4.4; Cl, 5.5; found: C, 69.2; H, 5.9; N, 4.5; Cl, 5.5.

3.11. Dyes **13a**,**b**. General procedure

The mixture of **9a**,**b** (1 mmol) and 4-dimethylaminobenzaldehyde (1.2 mmol) in acetic anhydride (2 ml) was refluxed for 1 min.

3.12. 3-Diethylamino-9-[2-(4-dimethylaminophenyl)-vinyl]-6-methoxyxanthylium perchlorate (**13a**)

After cooling, the resulting precipitate was filtered off and washed with acetic acid. Yield: 50%. M.p. = 219–220 °C.

^{1}H NMR ($CDCl_3$), δ: 1.34 (6H, t, $J = 6.6$ Hz, CH_3), 3.1 (6H, s, NCH_3), 3.6 (4H, q, 7.4 Hz, NCH_2), 3.98 (3H, s, OCH_3), 6.68 (1H, s, H^4), 6.76 (2H, br d, ArH), 7.00 (1H, s, H^5), 7.08 (1H, d, $J = 9.3$ Hz, H^2), 7.17 (1H, d, $J = 9.6$ Hz, H^7), 7.37 (1H, d, $J = 15.3$ Hz, β-CH), 7.48 (1H, d, $J = 15.9$ Hz, α-CH), 7.69 (2H, d, $J = 9.0$ Hz, ArH), 8.07 (2H, d, $J = 9.3$ Hz, $H^1 + H^8$). Anal. ($C_{28}H_{31}ClN_2O_6$) calcd.: C, 63.8; H, 5.9; N, 5.3; Cl, 6.7; found: C, 63.6; H, 5.9; N, 5.4; Cl, 6.6.

3.13. 3-Diethylamino-9-[2-(4-dimethylaminophenyl)-vinyl]xanthylium perchlorate (**13b**)

After cooling, diethyl ether (40 ml) was added and then decanted from the resulting oily precipitate. The oil was recrystallized from ethanol. Yield: 37%. M.p. = 191 °C.

^{1}H NMR ($CDCl_3$), δ: 1.35 (6H, t, $J = 6.8$ Hz, CH_3), 3.1 (6H, s, NCH_3), 3.7 (4H, q, 7.2 Hz, NCH_2), 6.66 (1H, s, H^4), 6.68 (2H, d, $J = 9.3$ Hz, ArH), 7.27 (1H, d, $J = 9.6$ Hz, H^2), 7.45–7.58 (3H, m, $H^5 + H^7 + \alpha$-CH), 7.64 (1H, d, $J = 15.3$ Hz, β-CH), 7.68–7.80 (2H, m, H^6 + ArH), 8.14–8.24 (2H, m, $H^1 + H^8$). Anal. ($C_{27}H_{29}ClN_2O_5$) calcd.: C, 65.3; H, 5.9; N, 5.6; Cl, 7.1; found: C, 65.7; H, 6.0; N, 5.5; Cl, 7.2.

*3.14. Dyes **14a**,**b**, **15a**,**b**, **17a**,**b**. General procedure*

The mixture of **9a**,**b** (1 mmol) and corresponding ω-aldehyde (1.2 mmol) in acetic anhydride (2 ml) was refluxed for 1 min.

*3.15. 3-Diethylamino-6-methoxy-9-[3-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)propenyl]-xanthylium perchlorate (**14a**)*

After cooling, diethyl ether (40 ml) was added and then decanted from the resulting oily precipitate. The latter was recrystallized from acetic acid. Yield: 54%. M.p. = 244–245 °C.

^{1}H NMR ($CDCl_3$), δ: 1.31 (6H, t, $J = 7.2$ Hz, CH_3), 1.66 (6H, s, $C(CH_3)_2$), 3.56 (4H, q, $J = 7.5$ Hz, NCH_2), 3.75 (3H, s, NCH_3), 3.95 (3H, s, OCH_3), 6.62 (1H, br s, H^4), 6.81 (1H, d, $J = 13.2$ Hz, γ-H), 6.89 (1H, s, H^5), 6.95 (2H, m, $H^2 + H^7$), 7.18 (1H, d, $J = 7.8$ Hz, H'^7), 7.25 (1H, t, $J = 7.5$ Hz, H'^5), 7.38 (3H, m, $H'^4 + H'^6 + \alpha$-H), 7.97 (1H, d, $J = 9.6$ Hz, H^1), 8.04 (1H, d, $J = 9.3$ Hz, H^8), 8.25 (1H, t, $J = 12.9$ Hz, β-H). Anal. ($C_{32}H_{35}ClN_2O_6$) calcd.: C, 66.4; H, 6.1; N, 4.8; Cl, 6.1; found: C, 65.9; H, 6.1; N, 4.6; Cl, 6.2.

*3.16. 3-Diethylamino-9-[3-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)propenyl]xanthylium perchlorate (**14b**)*

After cooling, diethyl ether (40 ml) was added and then decanted from the resulting oily precipitate. The latter was recrystallized from ethanol. Yield: 60%. M.p. = 151 °C.

^{1}H NMR ($CDCl_3$), δ: 1.30 (6H, t, $J = 7.2$ Hz, CH_3), 1.67 (6H, s, $C(CH_3)_2$), 3.54 (4H, q, $J = 6.9$ Hz, NCH_2), 3.83 (3H, s, NCH_3), 6.52 (1H, s, H^4), 6.89 (1H, d, $J = 9.3$ Hz, H^2), 6.98 (1H, d, $J = 14.1$ Hz, γ-H), 7.23 (1H, d, $J = 8.4$ Hz, H'^7), 7.30 (1H, d, $J = 7.2$ Hz, H'^4), 7.39 (4H, m, $H^5 + H^6 + H^7 + H'^5$), 7.49 (1H, d, $J = 12.3$ Hz, α-H), 7.61 (1H, t, $J = 8.7$ Hz, H'^6), 7.96 (1H, d, $J = 9.3$ Hz, H^1), 8.10 (1H, d, $J = 8.4$ Hz, H^8), 8.33 (1H, t, $J = 13.5$ Hz, β-H). Anal. ($C_{31}H_{33}ClN_2O_5$) calcd.: C, 67.8; H, 6.1; N, 5.1; Cl, 6.5; found: C, 68.0; H, 6.3; N, 5.1; Cl, 6.4.

*3.17. 3-Diethylamino-6-methoxy-9-[3-(3-methyl-3H-benzothiazol-2-ylidene)propenyl]xanthylium perchlorate (**15a**)*

After cooling, diethyl ether (40 ml) was added and then decanted from the resulting oily precipitate. The oil was dissolved in chloroform (4 ml) and then diethyl ether (40 ml) was added. The resulting precipitate was filtered off. Yield: 79%. M.p. = 150 °C.

^{1}H NMR ($CDCl_3$), δ: 1.25 (6H, t, $J = 6.9$ Hz, CH_3), 3.44 (4H, q, $J = 7.2$ Hz, NCH_2), 3.84 (3H, s, NCH_3), 3.85 (3H, s, OCH_3), 6.31 (1H, s, H^4), 6.64 (1H, s, H^5), 6.75 (1H, d, $J = 9.3$ Hz, H^2), 6.84 (1H, d, $J = 9.3$ Hz, H^7), 6.94 (1H, d, $J = 13.5$ Hz, γ-H), 7.03 (1H, d, $J = 12.6$ Hz, α-H), 7.26 (1H, t, $J = 7.5$ Hz, H'^5), 7.34 (1H, d, $J = 8.1$ Hz, H'^4), 7.42 (1H, t, $J = 7.5$ Hz, H'^6), 7.70 (2H, m, $H^1 + H'^7$), 7.79 (1H, d, $J = 8.7$ Hz, H^8), 7.94 (1H, t, $J = 12.9$ Hz, β-H). Anal. ($C_{29}H_{29}ClN_2O_6S$) calcd.: C, 61.2; H, 5.1; N, 4.9; Cl, 6.2; found: C, 61.3; H, 5.1; N, 4.9; Cl, 6.0.

*3.18. 3-Diethylamino-9-[3-(3-methyl-3H-benzothiazol-2-ylidene)propenyl]xanthylium perchlorate (**15b**)*

After cooling, diethyl ether (40 ml) was added and then decanted from the resulting oily precipitate. The residue was recrystallized from ethanol. Yield: 27%. M.p. = 156–159 °C.

^{1}H NMR ($CDCl_3$), δ: 1.24 (6H, t, CH_3CH_2), 3.42 (4H, q, NCH_2), 3.90 (3H, s, NCH_3), 6.28 (1H, s, H^4), 6.75 (1H, d, $J = 9$ Hz, H^2), 7.02 (1H, d, $J = 12$ Hz, α-H), 7.03 (1H, d, $J = 13.5$ Hz, γ-H), 7.12–7.22 (2H, m, $H'^7 + H'^5$), 7.28 (1H, m, H^7), 7.38 (1H, t, $J = 7.5$ Hz, H'^6), 7.42 (2H, m, $H^5 + H^6$), 7.61 (1H, d, $J = 9.3$ Hz, H^1), 7.74 (1H, d, $J = 7.5$ Hz, H'^4), 7.80 (1H, d, $J = 7.8$ Hz, H^8), 7.97 (1H, t, $J = 13.2$ Hz, β-H). Anal. ($C_{28}H_{27}ClN_2O_5S$) calcd.: C, 62.4; H, 5.1; N, 5.2; Cl, 6.6; found: C, 62.7; H, 5.2; N, 5.3; Cl, 6.6.

*3.19. 3-Diethylamino-9-[3-(2,6-diphenylpyran-4-ylidene)propenyl]-6-methoxyxanthylium perchlorate (**17a**)*

After cooling, diethyl ether (40 ml) was added and then decanted from the resulting oily precipitate. The oil was dissolved in chloroform (4 ml) and then diethyl ether (40 ml) was added. The resulting precipitate was filtered off. Yield: 70%. M.p. = 165 °C.

^{1}H NMR ($CDCl_3$), δ: 1.26 (6H, t, CH_3), 3.46 (4H, br d, NCH_2), 3.82 (3H, s, OCH_3), 6.18 (1H, s, H^4), 6.53 (1H, s, H^5), 6.62 (1H, d, $J = 12.9$ Hz, α-H), 6.89 (1H, d, $J = 8.1$ Hz, H^2), 7.03 (1H, d, $J = 7.8$ Hz, H^7), 7.15 (1H, d, $J = 13.5$ Hz, γ-H), 7.25–7.50 (10H, m, ArH), 7.84 (1H, s, H'^3), 7.87 (1H, s, H'^5), 7.97 (1H, d, $J = 9$ Hz, H^1), 7.99 (1H, d, $J = 9$ Hz, H^8), 8.10 (1H, t, $J = 12.9$ Hz, β-H). Anal. ($C_{38}H_{34}ClNO_7$) calcd.: C, 70.0; H, 5.3; N, 2.2; Cl, 5.4; found: C, 69.8; H, 5.4; N, 2.2; Cl, 5.4.

*3.20. 3-Diethylamino-9-[3-(2,6-diphenylpyran-4-ylidene)propenyl]xanthylium perchlorate (**17b**)*

After cooling, diethyl ether (40 ml) was added and then decanted from the resulting oily precipitate. The residue was recrystallized from ethanol. Yield: 41%. M.p. = 213 °C.

^{1}H NMR ($CDCl_3$), δ: 1.28 (6H, t, CH_3), 3.47 (4H, br d, NCH_2), 6.19 (1H, s, H^4), 6.85 (1H, d, $J = 13.2$ Hz, α-H),

7.0–7.6 (13H, m, γ-H + H^2 + H^5 + H^6 + H^7 + 10H^{Ph}), 8.0 (4H, m, H^1 + H^8 + H'^3 + H'^5), 8.27 (1H, t, J = 12.9 Hz, β-H). Anal. ($C_{37}H_{32}ClNO_6$) calcd.: C, 71.4; H, 5.2; N, 2.3; Cl, 5.7; found: C, 71.8; H, 5.1; N, 2.3; Cl, 5.8.

*3.21. Dyes **16a**,**b**. General procedure*

The mixture of **9a**,**b** (1 mmol), 1-methyl-2-(2-phenylaminovinyl)-quinolinium tosylate (1 mmol) and triethylamine (1 mmol) in acetic anhydride (2 ml) was refluxed for 2 min. After cooling, diethyl ether (40 ml) was added and then decanted from the resulting oily precipitate. The latter was recrystallized from acetic acid.

*3.22. 3-Diethylamino-6-methoxy-9-[3-(1-methyl-1H-quinolin-2-ylidene)propenyl]xanthylium perchlorate (**16a**)*

Yield: 30%. M.p. = 159–161 °C.

^{1}H NMR ($CDCl_3$), δ: 1.21 (6H, t, CH_3), 3.37 (4H, br d, NCH_2), 3.78 (3H, s, OCH_3), 3.91 (3H, s, NCH_3), 6.0–8.1 (15H, m). Anal. ($C_{31}H_{31}ClN_2O_6$) calcd.: C, 66.1; H, 5.6; N, 5.0; Cl, 6.3; found: C, 65.6; H, 5.8; N, 5.1; Cl, 6.1.

*3.23. 3-Diethylamino-9-[3-(1-methyl-1H-quinolin-2-ylidene)propenyl]xanthylium perchlorate (**16b**)*

Yield: 26%. M.p. = 175–177 °C.

^{1}H NMR ($CDCl_3$), δ: 1.29 (6H, t, CH_3), 3.50 (4H, br d, NCH_2), 4.15 (3H, s, NCH_3), 6.26 (1H, s, H^4), 6.9–8.3 (15H, m). Anal. ($C_{30}H_{29}ClN_2O_5$) calcd.: C, 67.6; H, 5.5; N, 5.3; Cl, 6.7; found: C, 67.9; H, 5.4; N, 5.3; Cl, 6.7.

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