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CYANINE DYES CONTAINING N-SUBSTITUTED AZAAROMATIC MOIETIES

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Syntheses and properties of cyanine dyes bearing N-substituted pyridine and quinoline rings, including cationic cyanines and merocyanines are reviewed.

INTRODUCTION

In a continuation of our experimental [1-4] and review [5-8] articles on azaaromatics, a subject of a current interest, the present paper deals with cyanine dyes bearing such systems.

Cyanines, especially those showing electro- and photochromic properties, deserve attention for their applications; they may be used in optical recording materials, as electronic photosensitizers as well as color electrophotographic processes [9-12]. Their application in photomemory systems [13], in information processing, and in monitoring of a neuronal network [13, 14] is also possible.

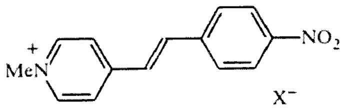
Solvatochromism of cyanine dyes allows us to use them as solvent polarity indicators [15, 16]; it should also be pointed out that cyanines absorbing in the near infrared region may be applied as photoreceptors of photodiode lasers [17-20]. A rapid development of the chemistry of cyanine dyes bearing N-substituted azaaromatics is observed; from a great variety of these species [21-27] some examples showing their synthetic approaches and properties will be described here.

To cyanine or polymethine dyes bearing N-substituted azaaromatic moieties belong cationic cyanines, i.e., quaternary salts of azaaromatics and merocyanines, i.e., azaaromatic betaines. In both groups species containing pyridine and quinoline moieties will be presented.

1. CATIONIC CYANINES

1.1. Cationic Cyanines Containing Pyridine Moieties

In describing synthetic approaches to cyanines, we should mention the synthesis of I performed by the quaternization of appropriate pyridines with methyl iodide and the subsequent exchange of iodide ion for tetraphenylborate, tosylate or perchlorate.



Ia–c

Ia X = BPh$_4$, b X = p-MeC$_6$H$_4$SO$_3$, c X = ClO$_4$

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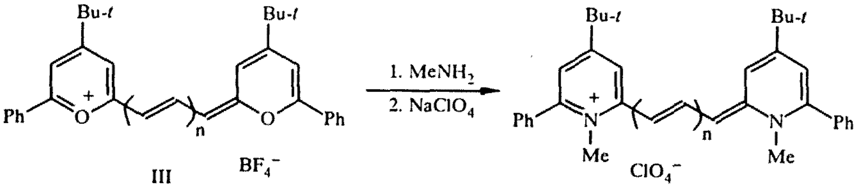
In the case of Ia strong second harmonic generation, about three times larger than that of urea was observed; it is due to the ion-pair CT transition between tetraphenylborate as electron donor and stilbazolium as electron acceptor. For Ib and Ic the second harmonic generation is weaker [28, 29].

The cyanine dyes II were synthesized from corresponding pyrylium salts III by treatment with methylamine [30].

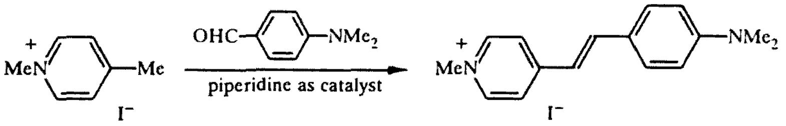


III

n = 1, 2

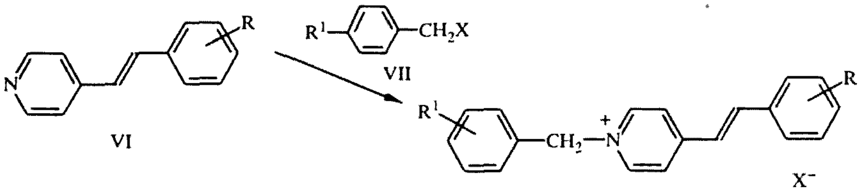
II

For the synthesis of IV the following procedure was used [31].



IV

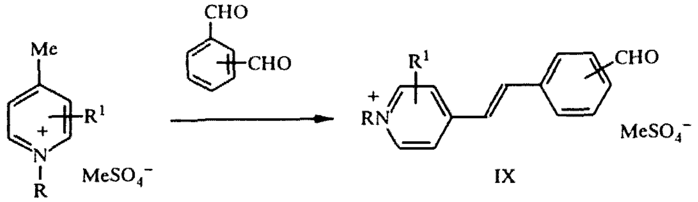
Cyanines V were obtained by quaternization of VI with benzyl halides VII [32].



V

VI R = 2-, 3-, 4-OH; VII R^1 = 2-Cl, 4-Cl, 4-Br, X = Cl, Br

The reaction of pyridinium salts VIII with benzenedicarboxaldehydes leads to photosensitive IX; quinoline analogues are obtained in a similar way [33, 34].

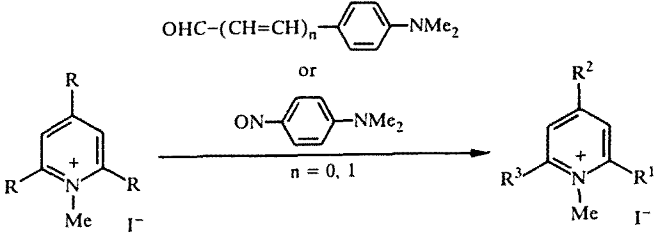


IX

VIII

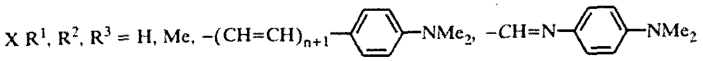
R = H, alkyl, aralkyl; R^1 = H, lower alkyl

Mono-, di-, and tricyanines and azomethines X have been synthesized by the condensation of methylpyridinium salts with aldehydes or nitroso compounds.



R = H, Me

X

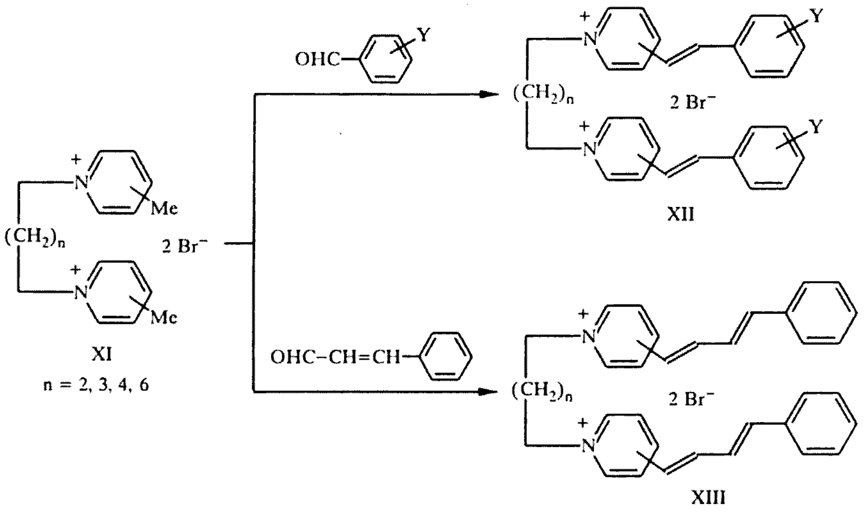


X R^1, R^2, R^3 = H, Me, $-(CH=CH)_{n+1}-C_6H_4-NMe_2$, $-CH=N-C_6H_4-NMe_2$

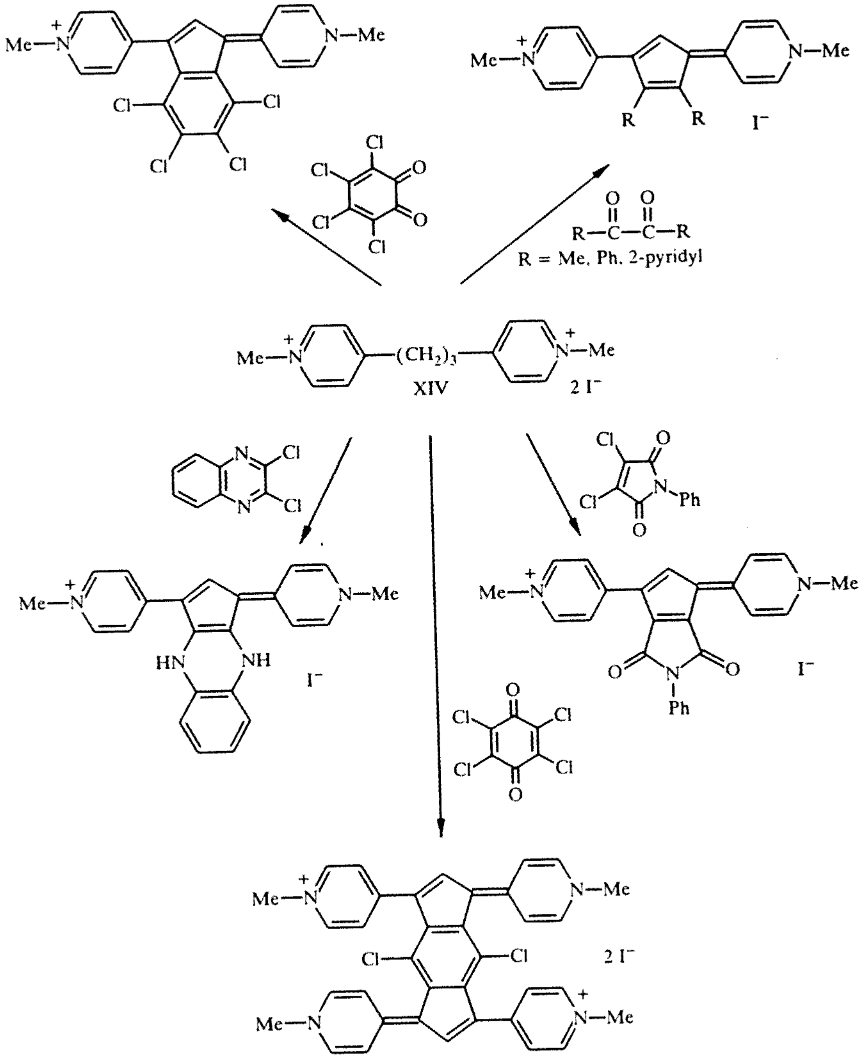
The dyes formed show negative solvatochromism. The considerable bathochromic shift, increasing in the order mono- < di- < tri-cyanines and for groups $-CH{=}CH-$ < $-CH{=}CH-CH{=}CH-$ < $-CH{=}N-$ was observed [35].

The condensation of dipyridinium salt XI with substituted benzaldehydes or cinnamaldehyde affords bridged cyanines XII and XIII [36, 37].

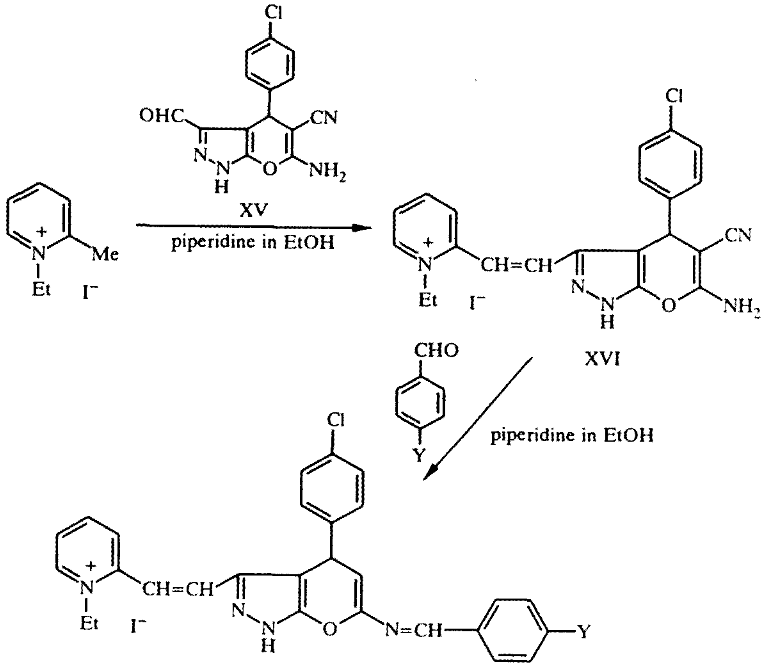
Cyanine dyes bridged by a cyclopentadiene ring are obtained in the following condensations of 1,3-bis(N-methyl-4-pyridinio)propane diiodide XIV [38, 39].



Y = H, 2-Cl, 4-Cl, 2-OH, 4-OMe, 4-NMe$_2$, 3-NO$_2$, 4-NO$_2$



The interaction of 1-ethyl-2-methyl pyridinium iodide with aldehyde XV gives rise to the dye XVI, converted by treatment with substituted benzaldehyde into the Schiff base XVII [40].

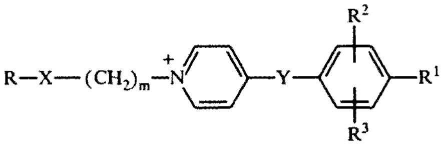


XVII

Y = Cl, OH, OMe, NO_2

Similar reactions were performed on 1-ethyl-2-methylquinolinium iodide [40].

Cyanines have interesting properties, e.g., XVIII are used in the preparation of nonlinear optical materials [41].



XVIII

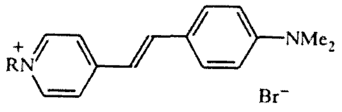
R = H, $n(CH_2)_t$, $H(CH_2)_tCO$, t = 0...25, X = O, S, NH; Y = CH=CH, —CH=N, —N=N—, m = 1...10;
R^1 = $H(CH_2)_nO$, $H(CH_2)_nS$, R^2,R^3 = $H(CH_2)_nO$, $H(CH_2)_nS$, n = 10...25

Cyanine XIXa, showing a large permanent dipole moment, is a nonlinear optical material exhibiting a considerable second harmonic generation, due to its high hyperpolarizability in the crystalline state [42, 43].

The pulsed electric birefringence and dichroism of XIXa were measured in the presence of poly(p-styrenesulfonate) and poly(L-α-glutamate) in aqueous solutions [42].

The dye bearing a hydrophobic chain XIXb obtained by condensation of N-cetyl-4-methylpyridinium bromide with 4-N,N-dimethylaminobenzaldehyde may be used as a probe in the investigation of solubilization sites in organized assemblies [44].

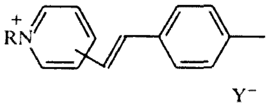
The effect of a systematic dilution on the aggregation of a hemicyanine dye XIXc in Langmuir–Blodgett film was examined by absorption spectroscopy [45]. At high concentration a second-order nonlinearity does not occur, this fact being a consequence of intermolecular interactions within the aggregate [45-50].



XIXa–c

XIXa R = Et, b R = C_9H_{19}, c R = $C_{22}H_{45}$

Water soluble polymers, e.g., poly(vinyl alcohol) containing photosensitive pyridinium or quinolinium groups of the type XX are used in positive-working photosensitive compositions which can be applied for printing plates [51].

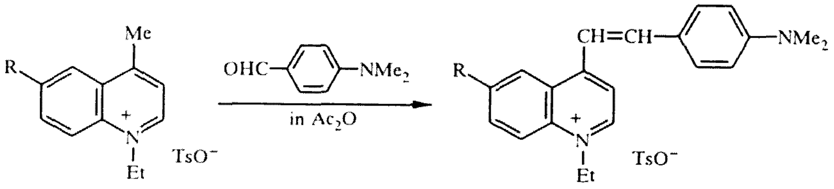


XX

R = alkyl, Y = anion

1.2. Cationic Cyanines Containing Quinoline Moieties

Among numerous cationic cyanines containing quinoline moieties [52, 53] we should mention dyes XXI synthesized in the following way [54]:

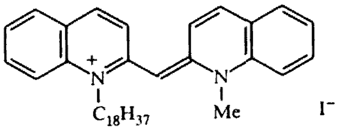


XXI

R = F, CF_3, SCF_3, $SOCF_3$, SO_2CF_3

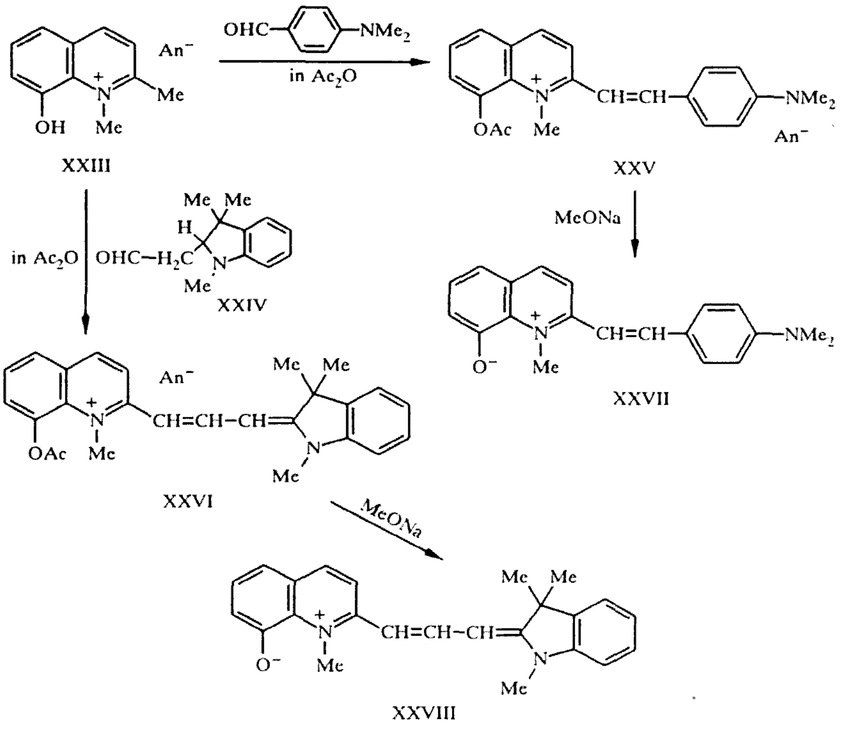
The presence of the fluorine-containing groups results in the bathochromic shift; XXI may be used as spectral sensitizers [54].

In the study of binary dye–surfactant system, and interaction within them, the cyanine XXII–stearic acid mixture has been investigated using various techniques; fluorescence microscopy allowed direct observation of the lateral structure formation in monolayers [55-60].



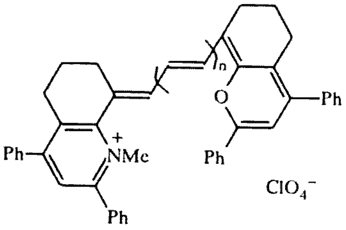
XXII

Reactions of quinolinium salt XXIII with 4-dimethylaminobenzaldehyde and aldehyde XXIV lead to cyanines XXV and XXVI converted by sodium methylate into zwitterionic dyes XXVII and XXVIII [61].



An = ClO_4, TsO

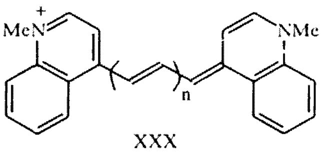
To cyanines containing quinoline moieties belong XXIX obtained from corresponding pyrylium salts by treatment with methylamine in dimethyl sulfoxide [62].



XXIX

n = 0, 1, 2

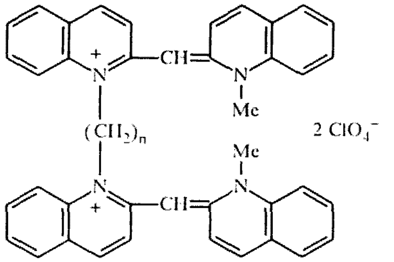
In cyanines XXX the bathochromic shift is observed with an increase of n from 0 to 3 [63].



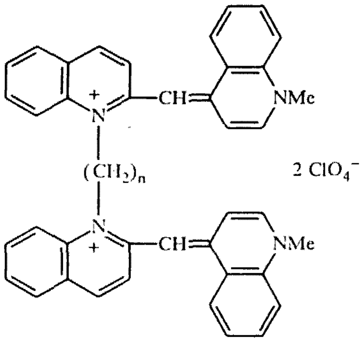
XXX

n = 0...3

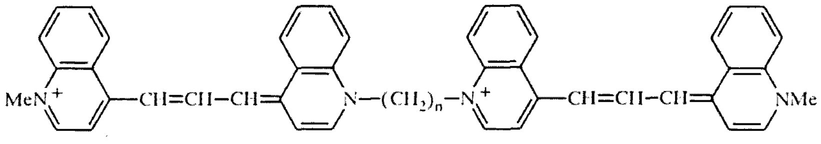
Examples of bridged dicyanines bearing quinoline moieties are salts XXXI, XXXII [64], and XXXIII [65].



XXXI



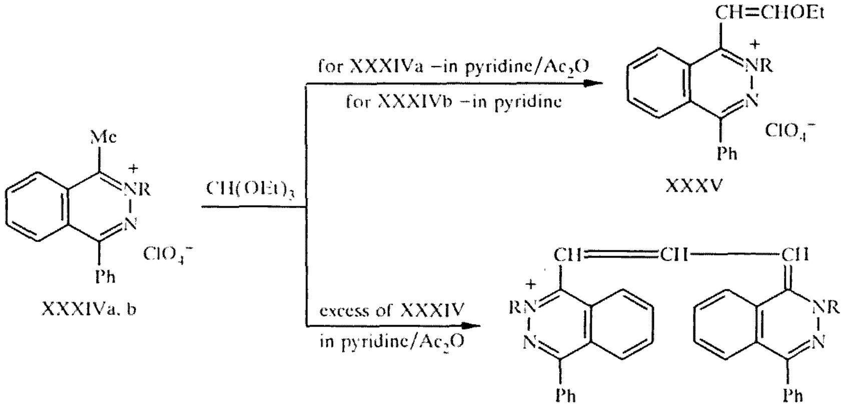
XXXII



XXXIII

n = 2, 10

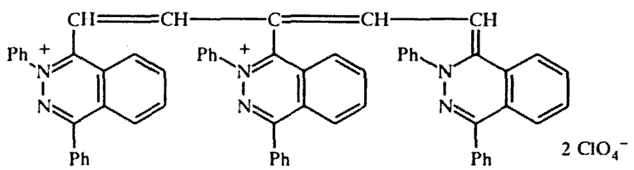
In the investigation of cyanines containing the phthalazinium system, the interaction of XXXIV with ethyl orthoformate was examined. The reaction carried out in pyridine/Ac$_2$O for XXXIVa and in pyridine for XXXIVb leads to XXXV, while an excess of ethyl orthoformate in pyridine/Ac$_2$O XXXVI is obtained [66].



XXXVI

XXXIVa R = Me, b R = Ph

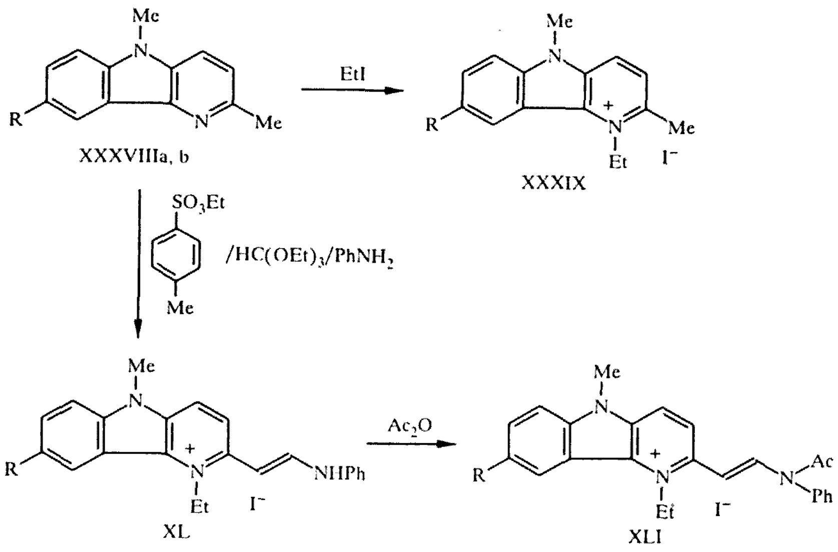
In reactions of XXXIVb, along with XXXVI also a small amount of XXXVII was formed.



XXXVII

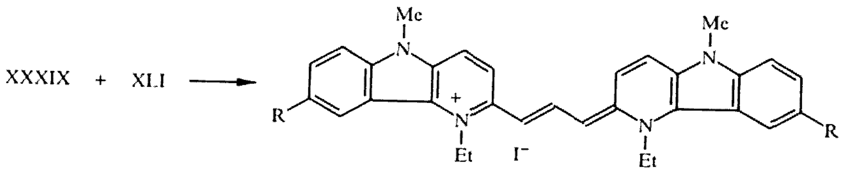
The observed bathochromic shift increases in order XXXV < XXXVI < XXXVII.

Studying cyanines containing indolopyridine systems, XXXVIII was treated with ethyl iodide to give XXXIX. The starting XXXVIII reacted also with ethyl p-toluenesulfonate, ethyl orthoformate, and aniline affording XL, converted by treatment with acetic anhydride into XLI.



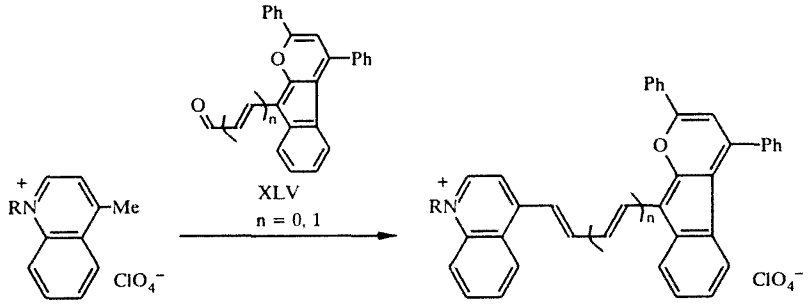
XXXVIIIa R = H, b R = Br

The condensation of XXXIX with XLI in DMSO in the presence of potassium t-butoxide leads to cyanines XLII [67, 68].



XLII

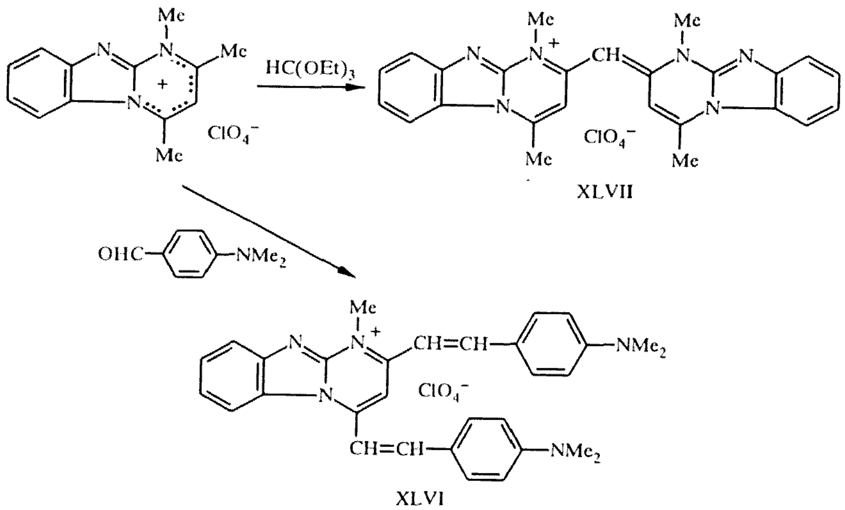
Cyanines XLIII have been obtained by treatment of quinolinium salt XLIV with aldehydes XLV, and their electron spectra were discussed [68].



XLIV

XLIII

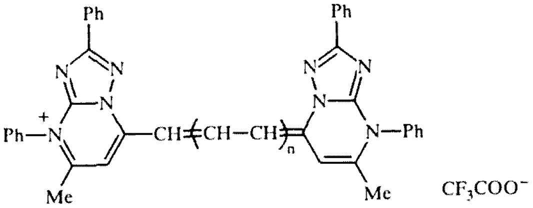
Dyes XLVI and XLVII have been synthesized in the following procedure [69].



XLVII

XLVI

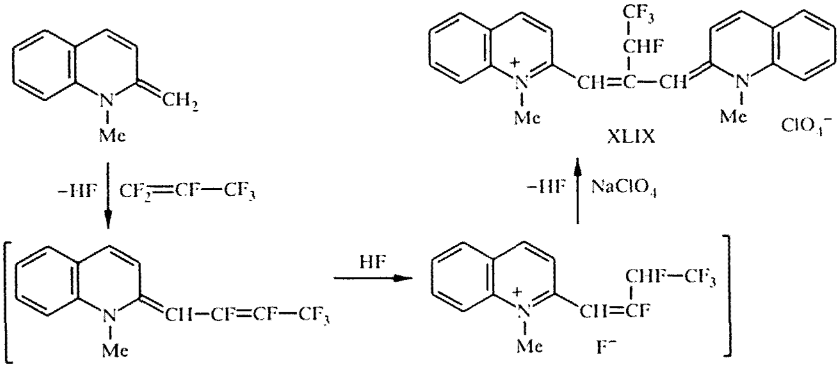
In a similar way cyanines XLVIII have been obtained [70].



XLVIII

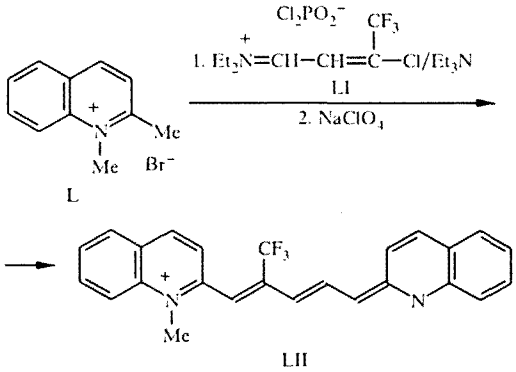
n = 1, 2

An example of the synthesis of cyanine bearing fluorinated substituent in the conjugated chain is the reaction of 1-methyl-2-methylene-2H-quinoline with perfluoropropene affording XLIX [70, 71].

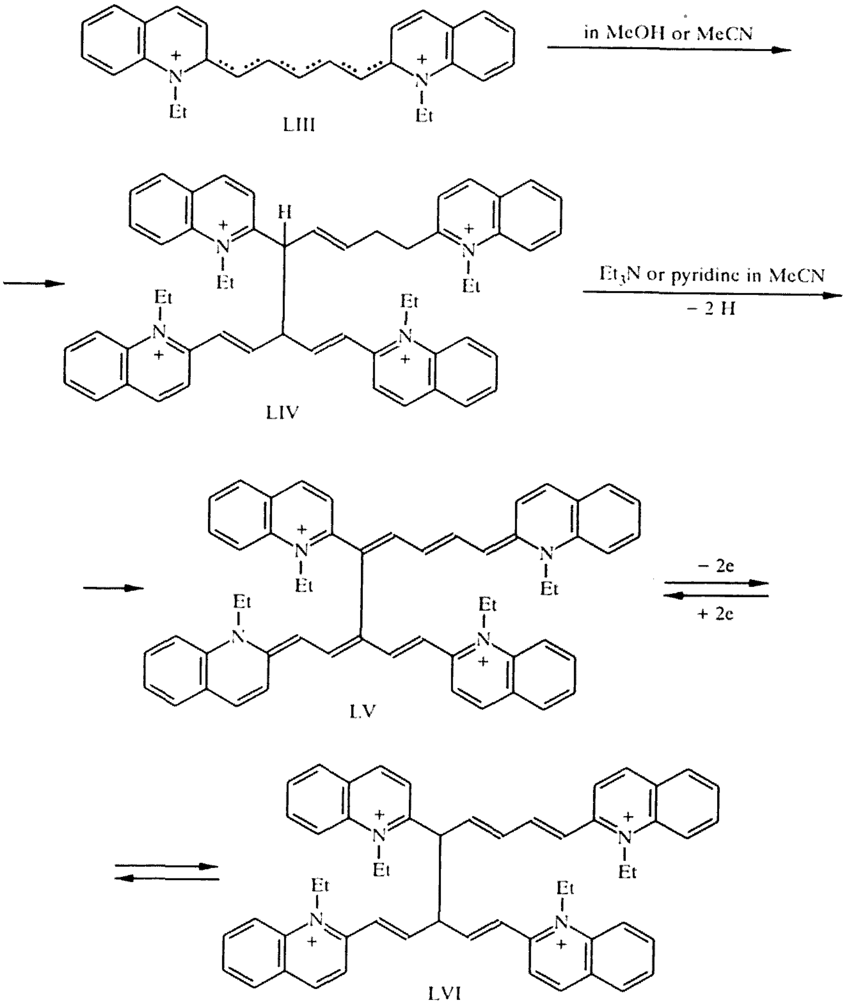


XLIX

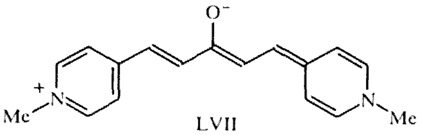
The quinolinium salt L reacts with azomethinium salt LI to give cyanines LII showing bathochromic shift due to the presence of trifluoromethyl group [72].



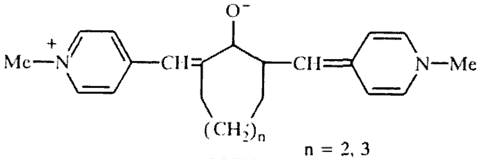
The dimerization of the radical dication LIII in methanol or acetonitrile was examined; this irreversible process leads to tetracation LIV. The deprotonation of the dimer LIV resulting in the dicationic bis-dye LV was performed in acetonitrile by the addition of a base (triethylamine or pyridine). The bis-dye LV may undergo a further oxidation via a reversible two-electron mechanism to afford tetracationic cross-conjugated species LVI [73].



To cyanines of a zwitterionic character bearing pyridine or quinoline systems belong compounds LVII, LVIII [75], LIX [75], LX [76], LXI, and LXII [77].

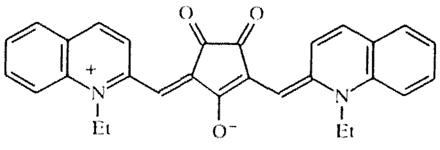


LVII

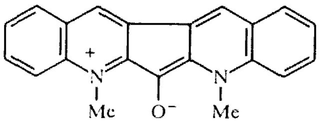


LVIII

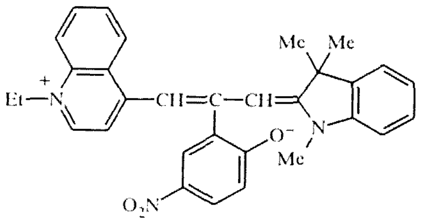
n = 2, 3



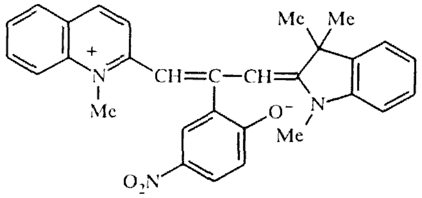
LX



LIX



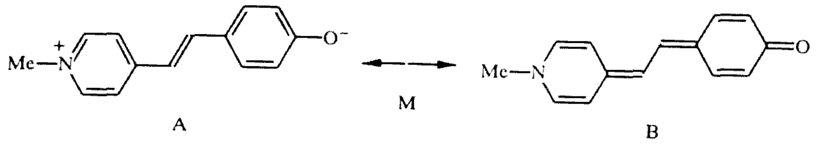
LXI



LXII

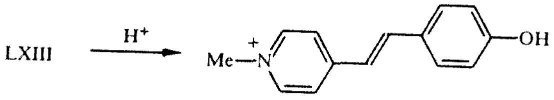
2. MEROCYANINES

A typical merocyanine is stilbazolium betaine M (LXIII); it is a resonance hybrid of two structures: the benzenoid, dipolar A and the quinoide, uncharged B.



LXIII

With the higher solvent polarity the contribution of the structure A increases [78]. The protonation of M gives the protonated form MH [79].



M exhibits the photochemical isomerization between Z and E conformations. The study of SERRS spectra in various solvents has shown that M in polar solvents exists mainly in the E-conformation, while in nonpolar solvents both conformations are present.

However when M is absorbed on a silver colloid in acetonitrile, only the E-conformation is to be found [79, 80].

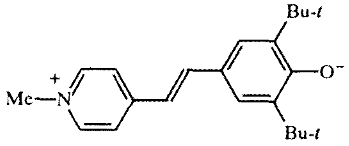
M shows the largest negative solvatochromism [78, 80-82]. The solvatochromism of merocyanines of this type permits their use as sensitizers in color photography, and due to their strong, solvent dependent hyperpolarizability their application in nonlinear optics [78, 83]. M shows a protolytic/photochemical reaction cycle, which may be of use as a chemical model for the storage of information and the subsequent regeneration of information carrier in biological systems [78].

$$\begin{tikzcd}
(Z)\text{-MH}^+ \arrow[r, shift left, "-H^+"] \arrow[d, shift left, "h\nu'"] & (Z)\text{-M} \arrow[l, shift left] \arrow[d, shift left, "\Delta"] \\
(E)\text{-MH}^+ \arrow[r, shift left, "+H^+"] \arrow[u, shift left, "h\nu"] & (E)\text{-M} \arrow[l, shift left] \arrow[u, shift left, "h\nu"]
\end{tikzcd}$$

Such merocyanines are potential diagnostic and therapeutic agents [84].

In the study of dynamics of solvation it was observed that the time-dependent shifts in the fluorescence spectra of solvatochromic probe molecules, e.g., M in frozen polar solvents result from inhomogeneous kinetic mechanism and are not connected with the solvent relaxation [85-87].

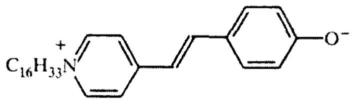
An example of merocyanines bearing bulky substituents is LXIV [78, 88]. The absorption and emission spectra of LXIV and of its protonated form have been measured in a variety of solvents. It was established that the effect of the solvent polarity is effaced, this fact being due to the presence of t-butyl groups [78].



LXIV

When alcoholic solution of LXIV is cooled to 77 K, a considerable thermochromism is observed [78].

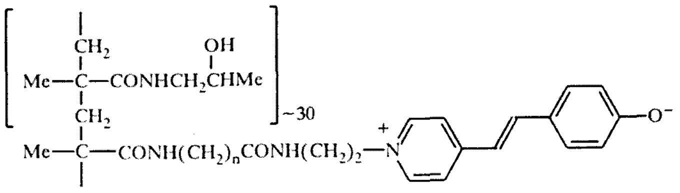
The solvatochromic visible absorption band of LXV can be utilized for estimation of interfacial solvent properties. Merocyanine LXV considered as solvatochromic acid–base indicator is suitable for quantitative measurement of the electrostatic surface potential of self-assembled surfactant aggregates in aqueous solutions [89].



LXV

Polymers of the type LXVI bearing at the end of side chains acidobasic groups exhibiting a solvatochromic absorption band were prepared [90].

The microenvironment of a solvatochromic reporter depends on the distance of the reporter from the polymer backbone. It was established that pK_a of reporters bound at a medium side chain of six methylene groups is close to pK_a of a low-molecular model compound, while pK_a of a reporter bound close to the polymer backbone is by ca. one unit higher.

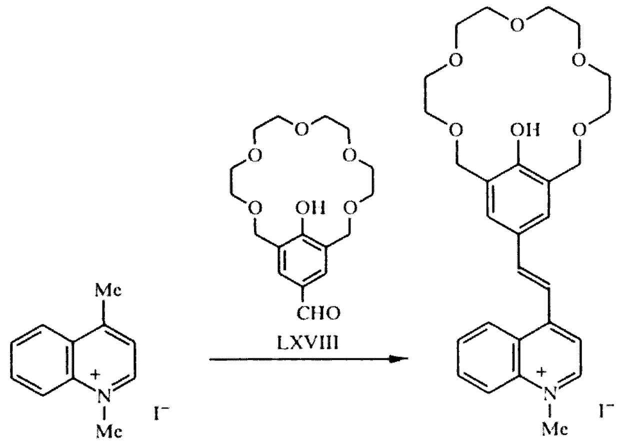


LXVI

n = 1...7, 11, 12

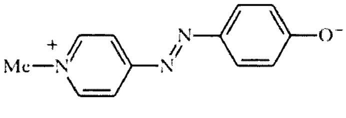
In the case of a larger number of methylene groups, the spacer is more hydrophobic, and intramolecular interactions of the long aliphatic chain occur. As a result, the immediate environment of the solvatochromic reporter becomes less polar, and the lower ionization constant of the reporter is observed along with the bathochromic shift of the sensitive solvatochromic absorption maximum [90].

Merocyanine dyes containing the crown ether system include LXVII, synthesized by coupling 1,4-dimethylquinolinium iodide with aldehyde LXVIII [91].

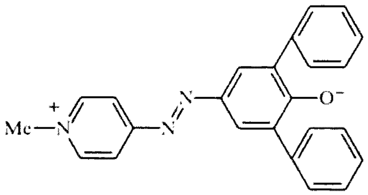


LXVII

Azomerocyanines should be mentioned here also; to this class belong LXIX and LXX; they show positive solvatochromism and may be applied in the formulation of a solvent polarity scale [92].

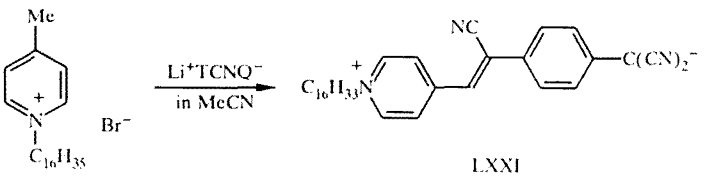


LXIX



LXX

An example of the merocyanine, where instead of O$^-$ another electronegative group is present, is LXXI, formed in the reaction of 1-hexadecyl-4-methylpyridinium bromide with Li$^+$ TCNQ$^-$ [93].



LXXI

Compounds of this type can find application as zwitterion photochromic species useful in Langmuir–Blodgett films [93].

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