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Merocyanine dyes: synthesis, structure, properties and applications

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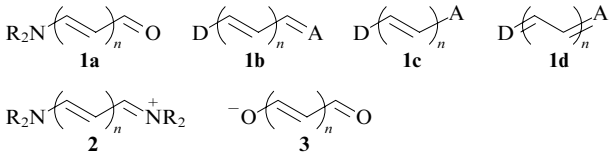
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Abstract. Key approaches to the synthesis of merocyanine dyes are summarised. The dependence of the dye properties on their chemical structure, the solvent nature and the aggregation type is analysed. The main methods of studying the electronic structure of merocyanines are considered. Attention is focused on polyene – polymethine electron transitions. The applications of merocyanines in modern research, including the design of new materials and technologies (non-linear optics, photovoltaics, holography, *etc*.) are presented. The bibliography includes 407 references.

I. Introduction

Merocyanines pertain to the class of polymethine dyes that continued to attract attention of scientists for more than hundred yeas. The first studies in this field were associated with the ability of polymethines to sensitise photographic silver halide emulsions in a wide spectral range.[1–4] The scientific progress in the second half of the 20th century, particularly, the discovery of lasers, considerably extended their application field.[5–13] Merocyanines belong to the group of so-called functional dyes,[14,15] their application field being determined by not only their colour, but also quite a number of other valuable properties.

In the classical definition,[1,5] the merocyanine class includes streptocyanines **1a** and their analogues in which both the nitrogen atom and the carbonyl group (or any other electron-withdrawing group containing a multiple carbon – heteroatom bond, *e.g.*, a nitrile group) can form part of a heterocyclic system. Like ionic cyanines, merocyanines contain two terminal heteroatoms and a polymethine chain (PC) in their chromophores.[7] Thus, merocyanines may be considered as a hybrid of two symmetrical dyes, cationic (**2**) and anionic (**3**) with PC of equal lengths. In contrast to ionic dyes **2** (chromophore charge +1) and **3** (charge −1), a merocyanine chromophore is electrically neutral.



The potential for modification of the chemical structures of the merocyanine terminal groups is substantially wider and structure **1a** does not cover many compounds of the merocyanine type containing non-classical electron-donating and(or) -withdrawing fragments. Hence, in the most general form, the term 'merocyanine' can be described as a 'polyene with a donor-and-acceptor substituents'[7,16] (structure **1b**, where D and A are the electron-donating and electron-withdrawing groups, respectively). However, when using this definition, it should be borne in mind that in contrast to usual polyenes, a merocyanine chromophore contains an odd number of carbon atoms in the conjugated π-system, which imparts the dye properties to this group of compounds. Merocyanines are often represented by structures **1c** and **1d**, which differ from **1b** in that their end electron-withdrawing or electron-donating groups include the neighbouring carbon atoms of the chain. It is convenient to use structures **1c** and **1d**, because for most merocyanines, the PC of an 'open' fragment (connecting its terminal hetero- and carbocyclic residues) contains an even number of methine groups.[1] Moreover, the division of these dyes to zero-, di-, tetra- and hexamethinemerocyanines, proposed in a classical review,[1] still holds.

Photophysical, photochemical and electrophysical properties of merocyanines, first of all, their clearly pronounced solvatochromism, their ability to substantially change their dipole moment upon excitation, to sensitise various physicochemical processes may be varied in a wide range by modifying the structures of both the end groups and the PC. Due to these properties, merocyanines have found their

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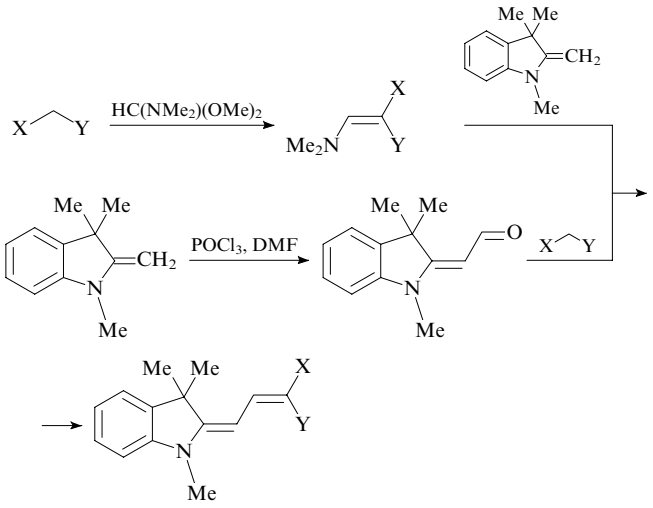
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application in designing new materials for optoelectronics, non-linear optics, optical carriers of information, solar concentrators and electroluminescent devices. They were also used as the fluorescent probes and markers in biological and medicinal studies, the promising antitumour agents in the photodynamic therapy, *etc*. As the donor-acceptor polyenes, merocyanines are perfect model compounds for the development of concepts on the electronic structure of conjugated systems, testing the potentials of modern quantum chemical methods of calculations.

A large number of publications on merocycanine dyes, especially those of recent years, require generalisation. In the known reviews [1,5,7,17–20] on polymethine dyes, merocyanines were presented together with compounds of other classes, which limited the possibilities for surveying their peculiarities. Moreover, most of the cited reviews were published more than 15 years ago. The latest review [10] on merocyanines cannot be considered comprehensive, because the only sufficiently thoroughly surveyed field was the synthesis of merocyanine dyes, particularly, the classical approaches, which were well described in previous reviews,[1,7] and little attention was paid to merocyanine properties, the problems of their interaction with the environment and also new application fields. The above considerations served as a stimulus for writing the present review.

II. Synthesis of merocyanine dyes

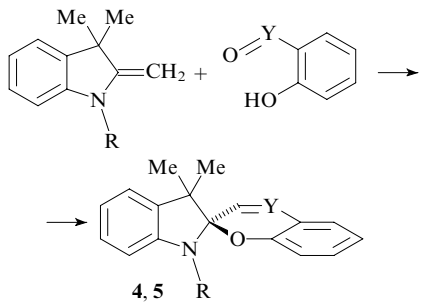
All the approaches to the synthesis of merocyanines relied on the so-called cyanine condensation.[1,10] An activated methylene group of a heterocycle (less common, the end groups are of carbocyclic or acyclic nature) serves as the nucleophile and a polymethine fragment containing the carbonyl group or its synthetic equivalents serves as the electrophile.[1–3,7,10] In the general case, the final step of the synthesis of merocyanines as non-symmetrical polymethine dyes includes the following two consecutive reactions: 1) condensation of a molecule bearing an end group with a polymethine fragment and 2) condensation of the resulting hemicyanine with the molecule containing second end group. Depending on the target molecule structure, synthesis could start from either a molecule with an electron-donating or -withdrawing group of the dye to be synthesised, which can be represented by, *e.g.*, the following scheme:



The applicability of one or another method is determined, first of all, by the nature of end groups, particularly, their donor-acceptor properties.[1,21,22] The main criteria of choice were the yield of the target compound and difficulties associated with its purification, *i.e.*, the amount of side products (these mainly included the corresponding symmetrical cationic and anionic dyes and vinylogues of the target merocyanines) should be minimised.

Thus, the synthesis of donor-acceptor polyenes faces two problems, namely, the synthesis of precursors and choice of the order in which cyanine condensations should be carried out.

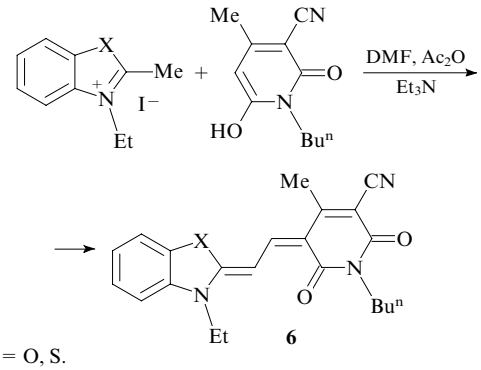
The problem is substantially simplified for merocyanines with short PC for which the corresponding aldehydes are readily accessible and also for zeromethinemerocyanines (which contain no spacer between the end groups).[6,10,23–28] A wide spectrum of accessible synthons that contain a methine group necessary for building the dye molecules are known, namely, esters, orthoesters, amidines, dialkylamides, *etc*.[1,2,25]. Using accessible aldehydes and *o*-hydroxy nitroso compounds, spiropyrans **4** and spiroxazines **5** that can exist in both closed (spiro-) and open (merocyanine) forms were also synthesised.[5,29]



4, 5

R = Alk; Y = CH (**4**), N (**5**).

The synthesis of dimethinemerocyanines (for example, dye **6**) is accompanied by a smaller number of side processes and, in contrast to higher vinylogues, they can often be prepared in one step.[25]



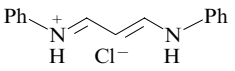
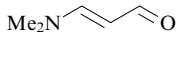
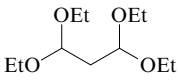
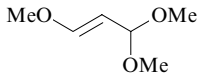
6

X = O, S.

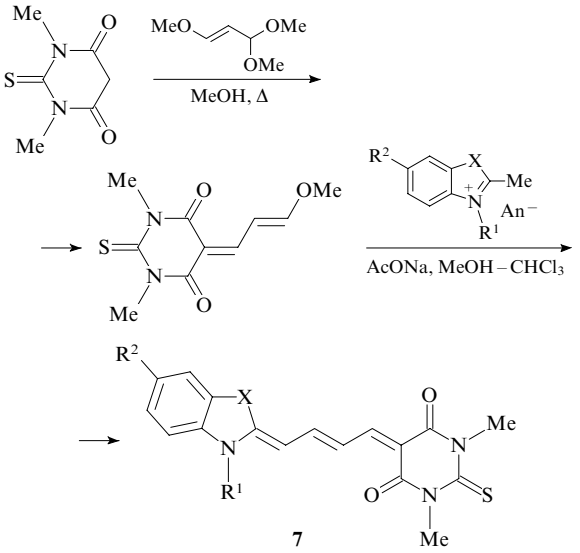
It is for this reason that dyes with short PC were studied in most detail and are used more often than their higher vinylogues.

The synthesis of merocyanines with longer PC is faced, on the one hand, with the larger number of side reactions [24] and, on the other hand, with the lesser accessibility of the starting compounds.

For tetramethinemerocyanines, different derivatives of malonaldehyde served as the accessible equivalents of three methine groups.[1, 2, 30]

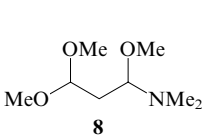
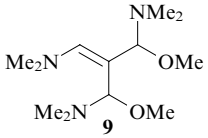
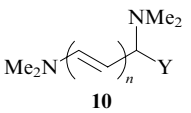
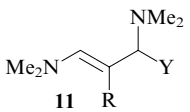





As an example, a scheme of synthesis of merocyanines **7** can be shown.



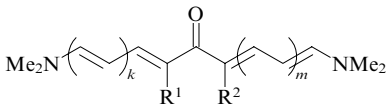
X = S, CMe_2; R^1 = Me, Et, $(CH_2)_3SO_3^-$, $(CH_2)_3\overset{+}{N}Me_2(CH_2)_2NCS$; R^2 = H, H_2N, FmocNH, $ICH_2C(O)NH$, AcNH; An = ClO_4, Br; Fmoc is 9*H*-fluoren-9-ylmethoxycarbonyl.

Compounds **8**–**11**, the derivatives of malonaldehyde, its heteroanalogues and vinylogues, offer great possibilities for the synthesis of various polyfunctional conjugated systems, particularly, merocyanines, based on the developed approaches.[31–35]


8

9

10

11

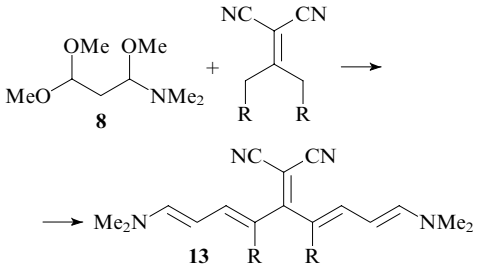
n = 1–4; Y = OMe, NMe_2; R = H, Hal, CN, Me, Pr^i, Ph, OEt, NMe_2.

Reactions of compounds **8**–**11** with aliphatic (including cyclic) unsaturated and heterocyclic ketones, diketones and other CH-acids afforded various functionalised polyenes of which many were formed in unusual chemical reactions.[31] A special place among such compounds is occupied by ω,ω′-bis(dialkylaminopolyenyl) ketones (ketocyanines) **12**, a representative of cross-conjugated bichromophore systems of the merocyanine type.


12

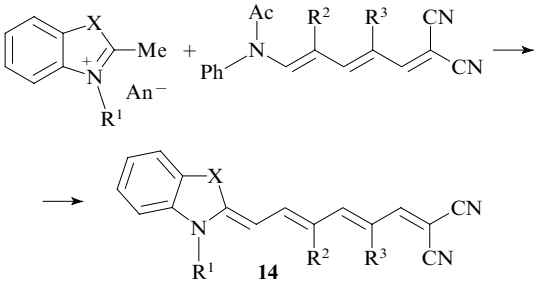
$R^1 = R^2$ = H; R^1 = H, R^2 = Me; $R^1 - R^2 = (CH_2)_n$ (*n* = 2–4), $(CH_2)_2CH(Me)$, $CH_2CH(Me)CH_2$, $CH_2CH(Me)CH(Me)$, $CH_2OCH(Me)$; *k* = 2–3, *m* = 2–4.

Based on compounds **8**–**11,** non-symmetric ketocyanines and diketocyanines were synthesised for the first time [31–33] as well as, dyes **13**, which are the analogues of ketocyanines with a malononitrile residue acting as the acceptor in place of the carbonyl group.[35]


8 **13**

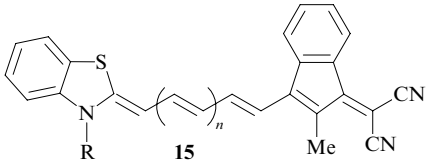
R – R = $(CH_2)_n$ (*n* = 3, 4).

Glutaconaldehyde derivatives served as the equivalent of five methine groups;[1, 36–39] as an example, the synthesis of dyes **14** can be shown.

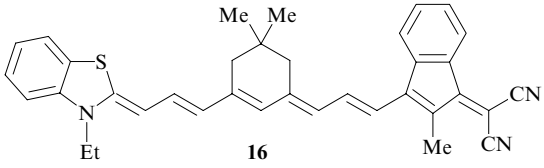

14

R^1 = Me, Et; $R^2 = R^3$ = H; $R^2 - R^3 = (CH_2)_3$, *o*-C_6H_4; X = S, CMe_2.

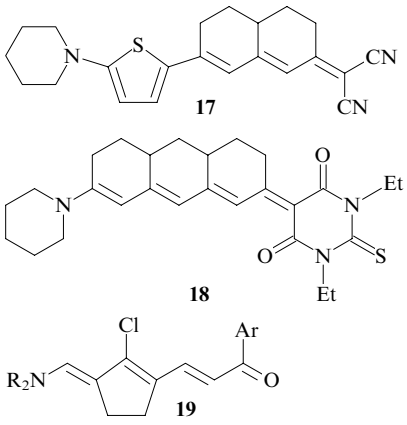
Further elongation of the merocyanine PC made their synthesis and isolation more difficult. Even hexamethinemerocyanines are relatively rare research subjects. Only few examples of the synthesis of merocyanines with longer PC (*e.g.*, compounds **15** and **16**) are known.[40]


15

R = Et, *n* = 0, 1; R = n-$C_{10}H_{21}$, *n* = 2.


16

As can be seen, dyes **15** and **16** contain at least one cyclic fragment in the PC. This is by no means accidental, the presence of these fragments in the chromophore of a polymethine dye favours its higher chemo-, thermo- and photostability and also the higher quantum yields of fluorescence.[11] Studies in this direction that have actively been developed in the USSR,[41] are still in progress. Many examples of such merocyanines (for example, compounds **17**–**19**) with the fixed conformation of the entire PC or its part are known.[14, 37, 38, 42–49]

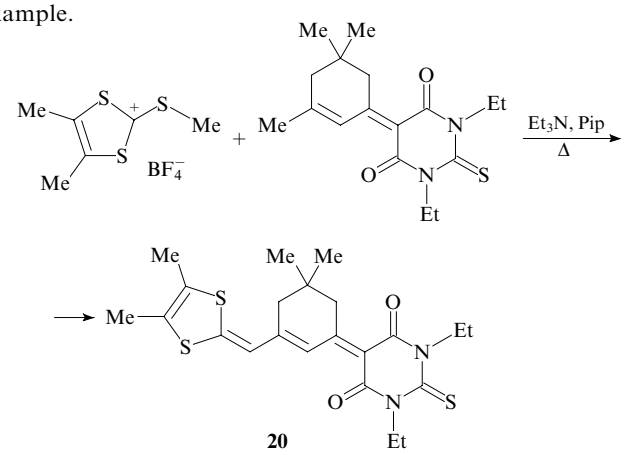


17 **18** **19**

R = Me, Et; R–R = $(CH_2)_5$; Ar = Ph, 2-naphthyl, 2-thienyl, *etc*.

Some of these compounds (for example, dyes **15** and **16**) absorb in the near IR region which is practically important.[8, 14, 40]

Schemes of merocyanine synthesis in which the reagent containing a PC fragment acts as the nucleophile were used albeit very rarely;[50] the synthesis of dye **20** can serve as an example.

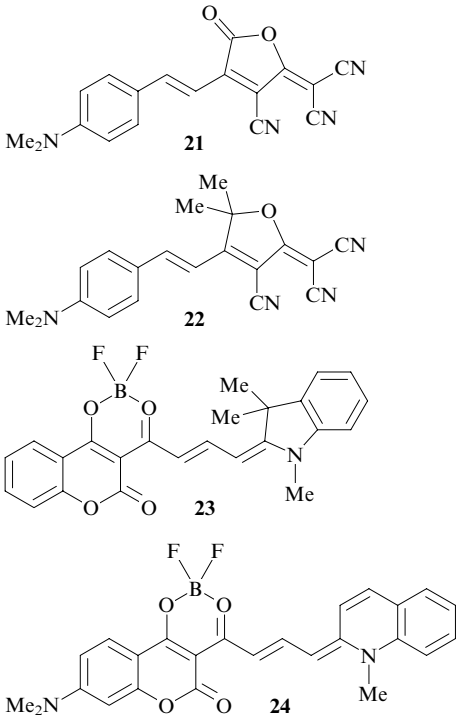


20

Pip is piperidine.

The 150-year history of chemistry of polymethine dyes witnesses that most of synthesised merocyanines represent the derivatives of heterocycles with a moderate electron-donating ability, namely, indole, benzothiazole, benzoxazole, 2-dialkylaminothiophene. Derivatives of stronger electron-donating heterocycles (*i.e.*, with higher basicity), namely, benzimidazole, pyridine, quinoline, are scarcer. Synthetic approaches to merocyanine dyes containing weak electron donors (*i.e.*, heterocycles with low basicity) are still less developed. For example, only few studies were devoted to merocyanines based on benzo[*cd*]indole,[21, 22, 51, 52] despite the higher effective length of its molecule that ensures the deep colour of the corresponding derivatives.

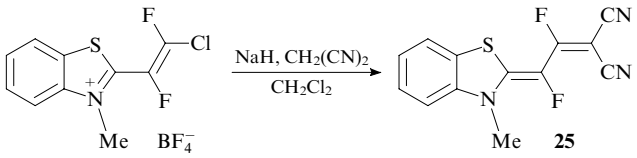
The range of electron-withdrawing units used in the synthesis of merocyanines is being extended. Among them, derivatives of strong acceptors of large effective length, for example, 3-cyano-2-dicyanomethylidene-4-methyl-2,5-dihydrofuran-5-one (**21**) and 3-cyano-2-dicyanomethylidene-5,5-dimethyl-2,5-dihydrofuran (**22**), deserve special attention[53] as well as difluoroborate complexes of 3-acetyl-4-hydroxycoumarins (**23**, **24**).[54–56]



21 **22** **23** **24**

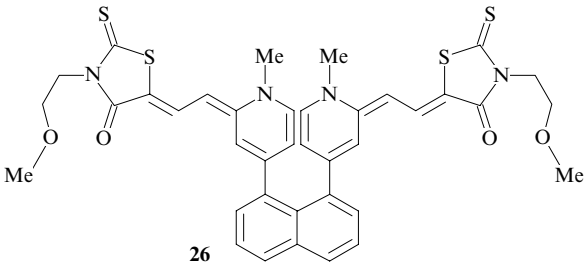
The synthesis of dyes that, in addition to the main chromophore, contain other functional fragments, such as coumarin,[24, 57] a long-lived aminoxide radical,[58] calixarene,[59] porphyrin,[60] a dicyanopyrazine fluorophore,[60] a photoconducting polyacetylene[61] is actively developed, which extended further the possible application fields of such dyes.

The development of new dyes and polyfunctional compounds with desired properties favoured the introduction of new synthetic methods into the chemistry of merocyanines. An interesting example illustrating the development of chemistry of merocyanines (polymethine dyes, in general) was a study[62] in which a series of compounds with the perfluorinated PC were synthesised (*e.g.*, dye **25**).

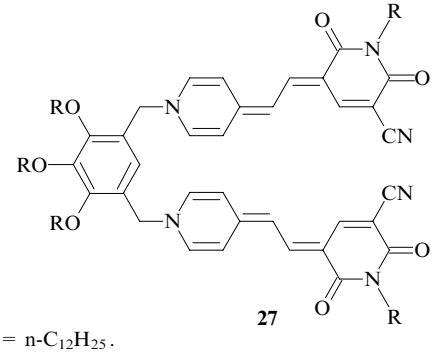


25

The synthesis of bis-dyes deserves special attention because they can serve as model compounds in studying the reactions of chromophores and the effect of aggregation processes on the spectra of dyes containing one chromophore. So far, only few publications were devoted to the synthesis and studies of bismerocyanines;[31–33, 47, 63–65] both compounds with sufficiently rigid geometry of chromophores (compound **26**) and with flexibly bound chromophores (**27**, **28**) were synthesised.

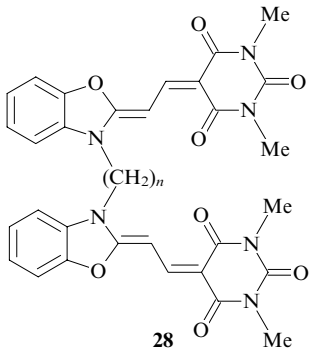


26



27

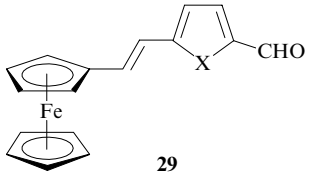
R = n-$C_{12}H_{25}$.



28

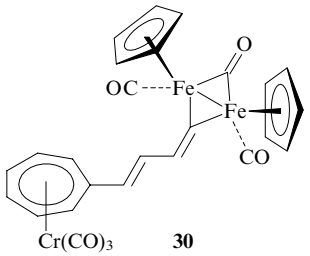
n = 3, 5.

New types of polyenes with donor-and-acceptor substitutents containing terminal groups unusual for such dyes, namely, organometallic (compounds **29**, **30**),[66–70] dithiafulvene,[71–74] polynitrofluorene (**31**), were synthesised.[68]

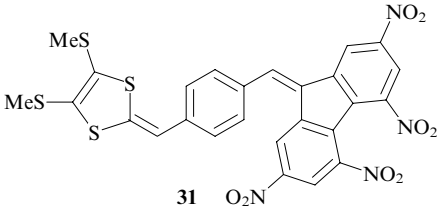


29

X = S, O.

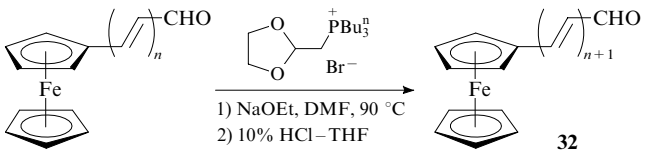


30



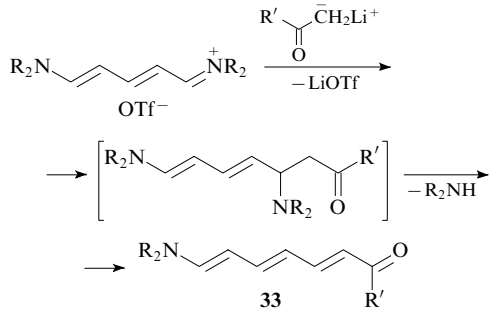
31

The value of these studies concerns not only the synthesis of new, often practically important compounds but also the elaboration of new approaches to the design of merocyanine chromophores. Thus an effective method of the PC elongation by two methine groups was described[66] by the example of dye **32**.



32

The lastest synthetic studies in the field of merocyanines tended towards the wider use of reactions involving organoelement compounds.[39,75] For example, an efficient one-pot synthesis of merocyanines **33** based on the reaction of the pentamethinium salts with organolithium reagents prepared from methyl aryl or methyl hetaryl ketones was developed.[76]



33

NR_2 = , NEt_2; R′ = Ar.

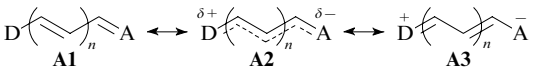
The most important step of the synthesis of non-symmetric polymethines is the isolation of an intermediate hemicyanine. Its purification and purification of the target dye is a sufficiently laborious problem that requires sophisticated chromatographic separation of the reaction mixture. Hence, the use of solid-phase synthetic methods seems a promising way of preparation of merocyanines.[39,77–79] Of the two main strategies, one includes the immobilisation of pre-synthesised hemicyanine on a polymeric solid phase[39,78] and the other, immobilisation of precursors for the subsequent synthesis of hemicyanines.[77]

III. Structure and fluorescence-spectral properties of merocyanine dyes

1. Electronic structure of merocyanines

The electronic structure of merocyanines can vary considerably depending on their chemical composition and the solvent nature. Merocyanines are the systems with the intramolecular charge transfer between the electron-donating and -withdrawing end groups along the conjugated bonds in PC. In this case, the term means a fictitious shift of the charge (electron) density in a molecule between a hypothetic resonance structure and the real electronic structure of the molecule, which in terms of the classical resonance theory is described by a linear combination of limiting resonance structures. It was proposed[7] to describe the electronic structure of merocyanines using the superposition of three basic limiting structures **A1** – **A3** that correspond to

three ideal states, namely, neutral polyene (**A1**), polymethine (**A2**) and bipolar polyene (**A3**).[7]



A1 **A2** **A3**

Depending on the structure of the end groups, the PC length and the solvent nature, merocyanines can approach any of their limiting states and also reside in states intermediate between **A1** and **A2**, **A2** and **A3**. Thus, their dipole moments can be increased (from **A1** to **A2** and further to **A3**) by changing their structures or by varying the solvent polarity.

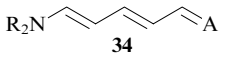
For the weakly pronounced electron-donating properties of group D and electron-withdrawing properties of group A, a merocyanine in the ground state S_0 approaches neutral structure **A1** that has zero π-charges on the chromophore atoms and the maximum alternating order of simple and multiple bonds in the conjugation chain. With the strengthening of either electron-donating properties of D or electron-withdrawing properties of A or both at once, the charge separation in the dye molecule becomes more pronounced as a result of the electron density transfer from D to A along the system of conjugated bonds. As a result, the order of a single bonds increases and the order of a double bonds decreases. For a certain ratio of D and A characteristics and the appropriate degree of solvent polarity, there comes a point where the chromophore bonds become sesquialteral, *i.e*, the **A2** structure also called the cyanine limit is reached. Moreover, the bond levelling is accompanied by the maximum alternation of the positive and negative partial charges on the chromophore atoms. When the **A2** structure is reached, the π-electronic frame of the dye molecule is delocalised to a maximum, which was proved, particularly, by determining the dependence on the merocyanine specific polarisability on the medium polarity.[7,80] With the further enhancement of the electron-donating and -withdrawing properties of D and A moieties, the charge separation becomes more pronounced and the bonds change their order to the opposite (structure **A3**) with respect to structure **A1**. Eventually, a bipolar polyene structure is reached, which is characterised by the maximum separation of opposite π-charges on terminal groups and the alternation of single and double bonds opposite to that in structure **A1**. This model was confirmed by NMR, IR and electronic spectra of polymethine dyes. Several direct evidences of polyene–polymethine transitions were obtained using the X-ray diffraction analysis.[7]

It deserves mention that within the framework of the scheme of three states **A1**–**A2**–**A3**, the choice of the electron-donating and -withdrawing groups in a merocyanine molecule may be arbitrary, because their electron-donating and -withdrawing properties degenerate upon reaching state **A2**.[81] When going from structure **A1** to **A3**, the donor-acceptor properties of these groups are in fact inverted.

The scheme proposed is a classical resonance model of valence bonds, because structure **A2** can be considered as a state with equal contributions of limiting structures **A1** and **A3**. The reason for singling out the cyanine limit is explained by the unique properties of merocyanines in this state.[7,16] First of all, the first electron transition to state **A2** corresponds to the longest wavelength, *i.e*., is characterised by the minimum excitation energy. Such a transition is accompanied by the smallest changes in the bond order, because in structure **A2**, in contrast to structures **A1** and **A3**, the order can change only from sesquialteral to double or single. As a result, the vibronic interactions of polymethines are weaker as compared with both types of polyenes, which leads to the narrowing of absorption and fluorescence bands, changes in their shapes and increase in the peak intensity (absorptance); the approach to **A2** structure favours the increase in the quantum yield of fluorescence (Φ_f) of merocyanines.[7,46,82] The levelled-out bond orders in the PC of structure **A2** hinder the photoisomerisation by rotation around bonds in the chain as compared with structures **A1** and **A3**.[7]

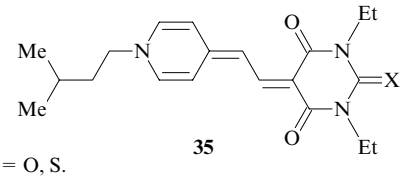
Upon the electronic excitation, the dipole moment of a dye molecule considerably increases, provided the ground-state structure lies in the interval between **A1** and **A2**, and decreases, if it lies between **A2** and **A3**. Hence, if the electronic structure of a merocyanine deviates from structure **A2**, a considerable charge transfer occurs in its molecule upon excitation. For structure **A2**, the dipole moment remains virtually unchanged on excitation; moreover, the alternation of π-electron charges on the chromophore atoms is reversed. This situation was described[83] as the 'polymethine charge alternation' or the 'charge resonance'. Obviously, this was associated with the trend of a molecule to reach the energy-advantageous ideal state **A2** if only in the first excited state. Actually, for donor-acceptor systems, the superposition of the charge resonance and the light-induced charge transfer from one part of molecule to another was observed.[83]

The approach of the electronic structures of studied dyes to one of ideal structures **A1**, **A2** and **A3** can be judged from the degree of alternation of the bond lengths or orders in the chromophore. In the literature, to qualitatively assess the latter, the BLA (Bond Length Alternation) or BOA (Bond Order Alternation) parameters were used,[84–93] which were put forward by Marder based on the analysis of the structure of merocyanines described by the general schemes **34** and **35**.



34

A = O, $C(CN)_2$, cyclo-$C(C(O)NEt)_2C(O)$, cyclo-$C(C(O)NEt)_2C(S)$;
R = Alk.



35

X = O, S.

Parameters BLA and BOA represent the differences of average lengths or average π-orders between the formally single and double PC bonds. Parameter BLA is positive for the structures of the **A1** type and those intermediate between **A1** and **A2** (its maximum value for an ideal polyene is close to 0.11 Å, which corresponds to this parameter for cyclooctatetraene) and negative for **A3** and the structures in the **A2**–**A3** range.[84,85] Parameter BOA takes opposite signs (for cyclooctatetraene, it approaches −0.8). Both parameters tend to zero for structures of the **A2** type.

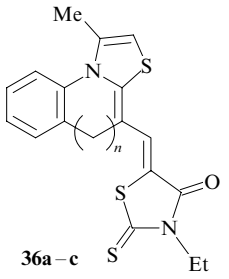
2. Absorption and fluorescence spectra

The directed quest for merocyanines with the predetermined properties required that the relationship of their electronic structure (position in the scale of structures **A1**–**A3**) with

the chemical structure of dyes and the solvent nature be elucidated. The most popular method of investigation of the electronic structure of dyes is studying their absorption and fluorescence spectra.

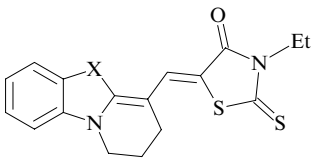
First studies devoted to the effect of the merocyanine chemical composition and the solvent polarity on their electronic absorption spectra were carried out in the 1950s–1960s by the groups of Brooker (*e.g.*, see Ref. 94) and Kiprianov (see Ref. 41). They have introduced a concept of 'deviation' that allowed Brooker to plot the first scale of the electron-donating and -withdrawing ability of end groups D and A.[95]

Kiprianov considerably extended the range of heterocycles used in the synthesis of polymethine dyes (*e.g.*, see structures **36a–c**, **37a–c**).[41] He studied the effect of PC substituents on the electronic structure and solvatochromism of merocyanines[41] and demonstrated its consistence with the Foester–Dewar–Knott rule.[95] Moreover, Kiprianov studied dyes with several chromophores, for example, rhodacyanines **38a–c** that attracted keen attention as the photoemulsion sensitisers.[3]



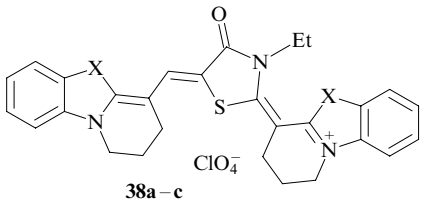
36a–c

n = 0 (**a**), 1 (**b**), 2 (**c**).



37a–c

X = CH_2 (**a**), O (**b**), S (**c**).

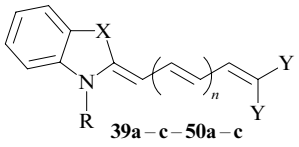


38a–c

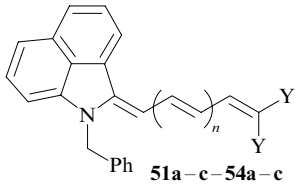
X = CH_2 (**a**), O (**b**), S (**c**).

Unfortunately, the approach to studying the spectral properties of merocyanines was not always systematic. The majority of publications were devoted to either individual merocyanines or rather narrow (as regards the variation of the donor-acceptor properties of terminal groups and the PC length) series of dyes.[46, 47, 73, 96–101] The scantiness (and often the absence) of the dye vinylogue series was probably associated with the aforementioned problems in the synthesis of polymethines with long PC. Moreover, in the analysis of the trends in electronic spectra of the dyes studied, the only reference points were the maxima of absorption or fluorescence bands (λ_{max}). However, the value λ_{max} did not always objectively reflect the spectral relationships, because the band maximum can be caused by different vibronic transitions.[11] The band maxima can be determined insufficiently accurately for broad, diffuse or strongly structured bands. Such changes in the curve shape are more typical of merocyanines than of the corresponding ionic dyes. The analysis of the band shape, first of all, their width, provides insight into the changes in the bond order and the electron density in a molecule that occur upon its excitation, which makes it possible to reveal the trends in the changes in vibronic and intermolecular interactions, respectively,[11] whereas λ_{max} for the most part allows one to elucidate the relative position of electronic levels of states S_0 and S_1^{FC}.

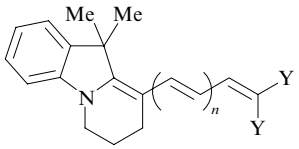
The regular changes in the electronic structure of merocyanines in the whole range of structures from **A1** to **A3** as a function of donor-acceptor properties of the terminal groups, the PC length and the solvent polarity were followed by the example of specially synthesised dyes with the smoothly varying electronic symmetry (**39–56**).[21, 22, 48, 52, 102]



39a–c–50a–c



51a–c–54a–c



55a–c, **56a–c**

39–42: X = CMe_2, R = Me;
43–46: X = S, R = Et;
47–50: X = NPh, R = Ph;
39, **43**, **47**, **51**, **55**: Y = CN;
40, **44**, **48**, **52**:
CY_2 = cyclo-$C(C(O)NH)_2C(O)$;
41, **45**, **49**, **53**:
CY_2 = cyclo-$C(C(O)NMe)_2C(O)$;
42, **46**, **50**, **54**, **56**:
CY_2 = cyclo-$C(C(O)NEt)_2C(S)$;
n = 0 (**a**), 1 (**b**), 2 (**c**).

For these structures, the mathematical analysis of the shape and width of spectral bands was carried out by the method of moments.[11] As a result, supplementary quantitative characteristics of the position and shape of bands (band centre, width, asymmetry, steepness and structuring) were obtained in addition to absorption peaks. The analysis of these characteristics together with such classical parameters as vinylene shifts and deviations made it possible to comprehensively characterise the electronic structure of these merocyanines (their position on the **A1–A3** scale of structures), and also its dependence on the chemical structure and the medium polarity. The found parameters, first of all, the widths of spectral bands made it possible to elucidate the type of merocyanine solvatochromism in those cases where this could not be inferred from λ_{max} values alone.

It was shown that in non-polar and weakly polar low-solvating solvents (n-hexane, toluene), the electronic structures of the ground state of all merocyanines under study fall into the **A1–A2** interval (see Refs 21, 22, 48, 52, 102), the increase in the PC length leading to the increase in the contribution made by the non-polar polyene structure **A1**. This follows particularly clearly from changes in the band shape, which for higher vinylogues ($n = 2$) resembles the band shape of typical polyenes, carotenoids (Fig. 1).

It is only for dyes **48–50** in which a strongly basic benzimidazole residue serves as the donor and a barbituric acid (or its derivative) residue acts as the acceptor that the state close to **A2** was reached even in low-solvating media.

In the series of merocyanines **39**, **41**, **42**, **47**, **49**, **50**, **54**, **55**, **56**, the polyene–polymethine transitions were analysed in more detail not only for their ground states but also for the first excited (fluorescence) states.[82, 103–107]

Note that the studies devoted to peculiarities of merocyanine fluorescence spectra are much fewer[47, 57, 108–120]

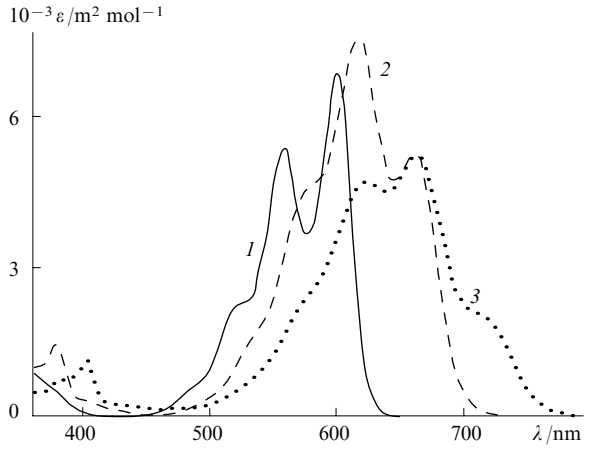


Figure 1. Electronic absorption spectra of dyes **54a** (*1*), **54b** (*2*) and **54c** (*3*) in n-hexane.[52]

than the studies of absorption spectra. Moreover, the systematic studies of dye series were scarcer than in the latter case. Such a situation can be explained primarily by experimental problems, namely, the low quantum yields of merocyanine fluorescence and the high requirements to purity of the samples, because the corresponding symmetric dyes formed in the merocyanine synthesis often exhibited higher Φ_f values.

Based on the classical mirror symmetry law for the absorption and fluorescence spectra, it could be expected that the trends in emission spectra of merocyanines will be the same as in their absorption spectra. The more so, it is surprising that in contrast to absorption spectra, the relationships observed in fluorescence spectra of typical electron-non-symmetric merocyanines[82, 104–107] were close to those of the corresponding symmetric dyes.[11] This was manifested in the virtual absence of deviations, the constancy of vinylene shifts and their approach to 100 nm, the narrowing of bands and their acquirement of the universal cyanine shape, the relatively weak dependences of emission spectra on the solvent polarity. This disturbed the mirror symmetry between the absorption and fluorescence spectra of merocyanines. Their mirror symmetry was retained when the ground-state merocyanne structure approached the structure of ideal polymethine **A2** and also in low-polar n-hexane, where the restructuring of the solvation shell in the excited state had no significant effect on the electronic structure relaxation of the dye.[82, 104–106]

3. Solvatochromism, solvatofluorochromism, thermochromism

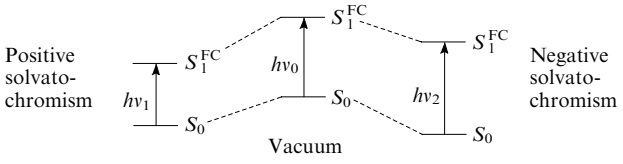
An important feature of merocyanines associated with the dynamics of electronic states **A1**–**A3** of their molecules is their pronounced solvatochromism,[121–128] *i.e.*, the electronic spectrum bands can change their position and shape with the solvent polarity. As was noted,[121] it is for merocyanine dyes that the solvatochromic properties were studied in most details.

Solvatochromism of organic dyes is caused by non-specific (universal) and specific interactions of their molecules with solvent molecules.[121] The former interactions are determined by macroscopic parameters of the medium, namely, the refractive index (n_D) and the dielectric permittivity (ε_D), whereas the latter interactions are determined by microscopic parameters [nucleophilicity (*B*) and electrophilicity (*E*)].[121]

The values of n_D and ε_D characterise the solvent polarisability and polarity, respectively. Non-specific dispersion interactions are associated with the appearance of instantaneous oscillating dipoles in the dye and solvent molecules and determined by polarisability of their molecules, which according to the Lorenz–Lorentz equation, is proportional to n_D. Parameter ε_D is associated with the orientation and induction interactions. It deserves mention that the strengthening of dispersion interactions of a substance with the environment, *i.e.*, the increase in n_D of the solvent always leads to the bathochromic shift of absorption and fluorescence bands. This is explained by the fact that the S_1 state is polarised stronger that the S_0 state; hence, the energy level of the former state decreases to the larger extent than the energy level of the latter with the increase in solvent n_D.

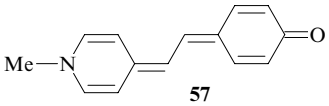
The macroscopic parameter ε_D does not reflect to the full extent the solvent polarity in the distributed-charge field of a dye molecule, because in this case the dye cannot be considered as a uniform continuous medium.[121] Under the action of the dye charge field, the solvent molecules in the first solvation shell are oriented in a definite fashion and, hence, subjected to the strongly non-uniform electric fields. The contribution of oriented molecules to the polar interactions, *i.e.*, specific electrostatic (polar) interactions of the distributed positive and negative charges in dye molecules with the negatively and positively charged ends of solvent molecule dipoles, is reflected to the considerable extent by the microscopic parameters *B* and *E*.

The increase in the dielectric permittivity of solvent and the strengthening of specific electrostatic interactions (parameters *E* and *B*), in contrast to dispersion interactions, can lead to both bathochromic and hypsochromic shifts of electronic spectral bands. The point is that solvation stabilises to different extent the ground (S_0) and excited (S_1^{FC}) states of the solute molecule with respect to vacuum. If the dipole moment of a molecule increased with the adsorption of a light quantum, then the polar solvent would more strongly reduce the energy of the excited state S_1^{FC}. This should lead to a bathochromic shift of the long wavelength absorption band (positive solvatochromism). If the dipole moment is larger in the dye's ground state, a hypsochromic shift is observed (negative solvatochromism).



On the other hand, if the transition from a certain solvent to both more polar and less polar solvents was accompanied by a hypsochromic shift of the electronic spectrum band, then we are dealing with the reverse solvatochromism (or the reversal of solvatochromism).[121, 129] This solvatochromism type was easily realised for merocyanines by selecting D and A groups such that the ideal polymethine state **A2** could be reached in a solvent of moderate polarity. Whereas both the decrease in the solvent polarity and its increase resulted in the shift from the ideal polymethine state to the uncharged polyene **A1** in the former case and to charged polyene **A3** in the latter case,

nonetheless, in both cases, the energy of the long wavelength electron transition increased.[7] The reverse solvatochromism was most thoroughly studied by the example of the Brooker merocyanine (**57**) and its analogues with different substituents at the nitrogen atom and in the oxyphenyl moiety.[118, 123, 130–136]

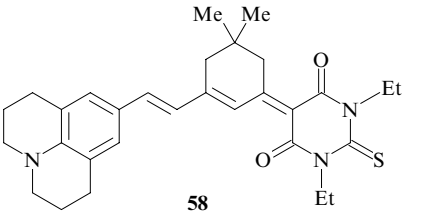


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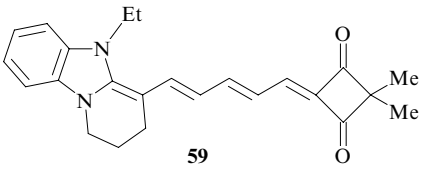
Everything noted above on the solvation is also valid for fluorescence spectra.

The role of additional parameters of the medium polarity, *e.g.*, electrophilicity and nucleophilicity, was to improve the agreement between the theoretical models of solvatochromism and practical results.[121] However, besides strongly complicating the development of theoretical models, the use of these parameters not always produced adequate results, because other factors, *e.g.*, the energy (entropy) of organisation of solvent molecules around a solute molecule, were ignored.

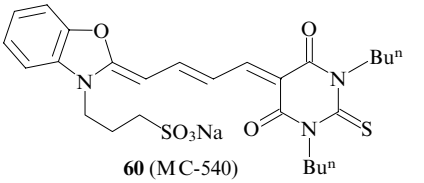
In practice, to describe the polarity of solvents, an alternative approach, namely, empirical equations based on the known solvation shifts for certain model compounds, was used. Several polarity scales were built in which the energy of the corresponding transition served as the main parameter (the Reichardt, Kosovert, Kamlet–Taft, Brooker scales, *etc.*).[121, 123, 137] Although many scales correlate well with one another, there is no universal scale of solvating ability, because different compounds interact in different manner with solvents. Merocyanines, for example, compounds **58**–**60**, have also found wide application in plotting the polarity scales.



58



59



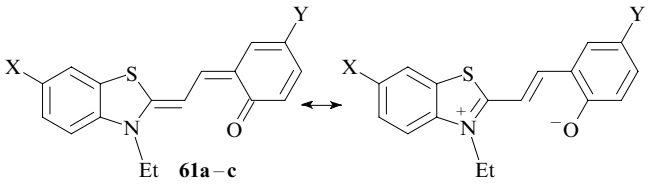
60 (MC-540)

All the mentioned scales are based on the ratio of free energies that relates the corresponding rate or equilibrium constants for different processes with certain, often artificial parameters for a series of compounds with similar compositions. This model is substantially simplified by considering a photon ($h\nu$) as the 'reagent' and the excited state of a substrate (S) in a medium (M) as the product.

$$S(M) + h\nu \rightleftharpoons S^*(M).$$

This 'reaction' depends only on two parameters, namely, the substrate structure and the nature of the medium.

The majority of merocyanines exhibit positive solvatochromism.[7, 138] For example, in a series of compounds **39**–**56**, almost two thirds of dyes (particularly, all derivatives of moderately electron-donating indole **39**–**42** and weakly electron-donating benzo[*cd*]indole **51**–**54**) were characterised by positive solvatochromism, compounds **48**–**50** were characterised by negative solvatochromism, and the rest exhibited reverse solvatochromism.[21, 22, 48, 52, 102] The reason for this lies in the fact that the realisation of a bipolar structure requires additional energy for the charge separation. This energy is supplied by the exciting light quanta; hence, this structure is easier realised in the excited state. However, the bipolar structure of merocyanines can be stabilised in the excited state too by the optimisation of the electronic structure of the molecule. Thus for dye **61a** with negative solvatochromism,[41] the bipolar structure of its ground state is advantageous for the following reasons: first, the oxyphenyl residue exhibits rather high acidity, which favours the localisation on it of a negative charge; second, its benzenoid structure has advantages over the quinonoid structure; and, third, in the bipolar structure, the thiazole ring is more aromatic (stable).



61a–**c**

X = Y = H (**a**); X = EtO, Y = NO_2 (**b**); X = NO_2, Y = EtO (**c**).

The reversal of the contribution of two limiting structures (positive solvatochromism) is reached upon the introduction of an electron-withdrawing nitro group into position 6 of the benzothiazole residue and an electron-donating ethoxy group into the *para*-position with respect to the oxygen atom of the oxyphenyl moiety (compound **61b**), *i.e.*, with the weakening of the electron-donating properties of the benzothiazole nucleus and the electron-withdrawing propeties of the oxyphenyl nucleus. At the same time, interchanging these groups led to dye **61c**, which is even more bipolar than compound **61a**, as confirmed by the increased solvatochromic shifts.

Recently, it has been found that the reversal of the solvatochromism sign can be reached not only by the change in the donor-acceptor characteristics of terminal fragments, but also due to the elongation of the PC.[22, 52] For example, for dye **46a**, the transition from toluene to dichloromethane was accompanied by a hypsochromic shift ($\Delta\lambda_{max}$ = 3 nm) and broadening of the absorption band (by 50 cm^{-1}), whereas for its vinylogue **46c,** a bathochromic shift ($\Delta\lambda_{max}$ = 17 nm) and substantial narrowing of the spectral band (by 350 cm^{-1}) were observed (Fig. 2), which was due to an increase in the contribution of structure **A1** and a decrease in the contribution of **A2** with the increase in *n*.[52]

The aforementioned problem often encountered in the literature, namely, the incorrect determination of the solvatochromism sign, can be illustrated by the example of absorption spectra of merocyanine **45b.** With the substitution of more polar ethanol for dichloromethane, λ_{max} of merocyanine **45b** underwent a hyprochromic shift rather

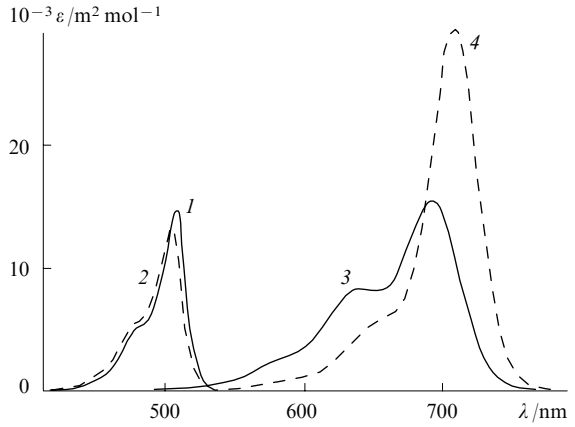
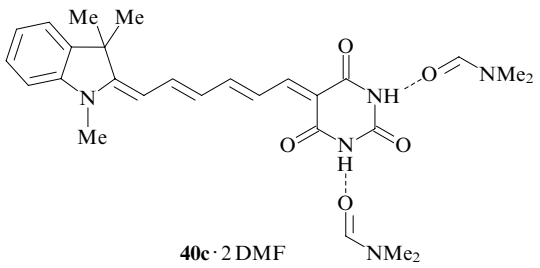


Figure 2. Electronic absorption spectra of dyes **46a** (*1*, *2*) and **46c** (*3*, *4*) in toluene (*1*, *3*) and dichloromethane (*2*, *4*).[52]

than bathochromic. Hence, it can be concluded that this dye exhibits negative solvatochromism. However, the transition to DMF was accompanied by a bathochromic shift of the long-wavelength band.[22] Hence, the hypsochromic shift with the transition to ethanol was associated with the lower n_D of ethanol as compared with dichloromethane, and this factor dominated in this case over the increase in the parameters ε_D, B, E with the transition to ethanol. This conclusion was confirmed by the regular narrowing of the absorption band of compound **45b** observed in the following series: dichloromethane, ethanol, DMF, which was only possible in the case of weakening of vibronic interactions. In turn, the latter was associated with the less pronounced bond order alternation, *i.e.*, the transition of the merocyanine structure towards **A2**.

Comparing dyes **39a**–**c** and **42a**–**c** with their close structural analogues **55a**–**c** and **56a**–**c** (Ref. 48) has shown that the presence of a trimethylene bridge (which in this case also behaved as an electron-donating substituent in the odd position of PC) not always leads to colour deepening. It was found that such a bridging group insignificantly increased the contribution of bipolar structures **A2** and **A3** to the electronic structure of merocyanines. This determines the extraordinary fact of variation of the solvatochromism type from positive in the series of compounds **42a**–**c** to the reverse in the series **56a**–**c**. The electron-donating cyclic group also weakened the charge alternation in the dye chromophore and, as a consequence, led to the weaker solvatochromism of dyes **55a**–**c** and **56a**–**c** as compared with compounds **39a**–**c** and **42a**–**c**, respectively.

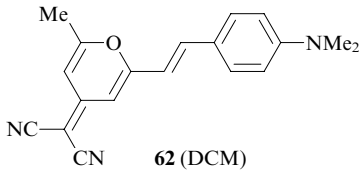
As was mentioned above, the increase in the medium polarity favoured separation of opposite signs in merocyanine molecules, which increased the contribution of bipolar structures **A2** and **A3**. However, it was shown[22] that this obvious rule has exceptions. For merocyanines **40a**–**c**, **44a**–**c**, **48a**–**c**, **52a**–**c**, *i.e.*, the derivatives of unsubstituted barbituric acid, the transition from dichloromethane to more polar DMF was accompanied not by the growth but, on the contrary, a decrease in the polarity of its molecules. It was shown that the formation of hydrogen bonds between the DMF carbonyl groups and the imide groups of the barbituric fragment led to the weakening of the electron-withdrawing properties of the latter, shifting the electronic structure of these merocyanines to nonpolar polyene **A1**, despite the high polarity of DMF.



40c · 2 DMF

A similar effect was probably observed for merocyanines **39a**–**c** and **51a**–**c** with the ground-state electronic structure approaching that of non-polar polyene **A1**. The donating fragment of their molecules (nitrogen atom that carries an unshared electron pair) could undergo electrophilic solvation in ethanol and acetonitrile, which increased the contribution of structure **A1**, despite the high polarity of these solvents.[21]

Solvatofluorochromism of merocyanines was studied only for individual compounds that have found wide application [for example, oxystyryl **57**,[118, 131] MC-540 (**60**)[113–115, 117, 119, 139, 140] and DCM dye (**62**)[141–143]] and were conventional subjects of theoretical studies.

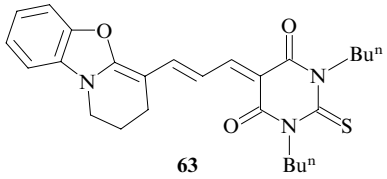


62 (DCM)

Systematic merocyanine series were studied.[46, 82, 103–107] It was shown that despite the general opinion that solvatofluorochromism manifests itself more strongly as compared with solvatochromism for zwitter-ionic dyes with the positive sign of the latter, the reverse situation was observed for many merocyanines. This was explained by the fact that their excited state approaches ideal polymethine **A2**, which leads to the weaker polar interactions with the solvent in this state as compared with the ground state.

It was shown that the increase in the solvent polarity for merocyanines with positive solvatochromism and its decrease for merocyanines with negative solvatocromism were accompanied by an increase in the quantum yields of fluorescence and a decrease in the Stokes shifts, because the fluorescence states of both dyes approached structure **A2**.[82, 103–107] These effects were associated with the weakening of vibronic interactions and the enhancement of the structure rigidity (with the lower probability of rotation around PC bonds) due to the weakening of alternation of bond orders and their approach to sesquialteral orders.

It is conventionally believed[7, 11, 46] that the introduction of cyclic groups into PC of polymethine dyes increases the quantum yield of fluorescence due to the increase in the structure rigidity. In was shown[144] that this rule is fulfilled by no means in all cases, for example, the value Φ_f of dye **63** was lower than that of its analogue **60** containing no tetrahydropyridine ring.



63

This problem was studied [107] by comparing dyes **55a–c** and **56a–c** with their analogues **39a–c** and **42a–c**. It was shown that the trimethylene bridge that connects the nitrogen atom of the indoline ring with the α-position in PC can both decrease and increase the quantum yield of fluorenscence. Moreover, the factors associated with the presence of this bridge that affect the value Φ_f (partial distortion of the planar molecular structure, facilitation of photoisomerisation processes and, in some cases, strengthening of vibronic interactions in fluorescence transitions) were substantially weakened with the increase in the PC length. The higher Φ_f values as compared with analogues containing no bridge were observed in those cases where the bridging group acting as a donor substituent in the PC brought the electronic structure of merocyanines close to that of ideal polymethine **A2**, which is typical of dyes with positive solvatochromism. And the other way round, when the ring disturbed the levelling of bond orders in the chromophore thus shifting the merocyanine structure to that of bipolar polyene **A3**, then a considerable increase in Φ_f values was observed. The latter was typical of merocyanines with the negative or reverse solvatochromism in strongly polar solvents.

Pulse fluorescence spectroscopy is currently the most popular method for studying photophysical properties of merocyanines (under the photophysical properties, the processes of relaxation of the dye molecule after its photoexcitation are meant).[100, 109, 114–117, 142, 145–170] In addition, methods of quantum chemistry,[148, 151, 155, 156, 159–161, 170] NMR spectroscopy,[148, 151, 170] Raman spectroscopy,[117, 171] ESR spectroscopy [172, 173] were used; the properties of dye complexes with cyclodextrins were studied.[174] These studies were most often focused on dyes MC-540 (**60**) and their derivatives,[114, 115, 117, 162–169] and also the Brooker merocyanine (**57**) and ketocyanines (**12**). The processes of *trans–cis*-photoisomerisation,[147, 163] the formation of TICT states (Twisted Intramolecular Charge Transfer),[149, 153] the merocyanine photostability[100] were studied in sufficient details.

As a special case of solvatochromism and solvatofluorochromism of merocyanines, their thermochromism[63, 96, 110, 136, 175–178] can be considered, *i.e.*, the dependence of the absorption and fluorescence spectra on the temperature. It was shown that the observed thermochromic effects were associated with both the dependence of macroscopic parameters of solvent polarity on the temperature and the stronger ordering of the solvation shell at low temperatures and its distortion at higher temperatures.[96, 176] For merocyanines **39a–c** with positive solvatochromism, it was found that a decrease in the temperature led to a bathochromic shift of absorption bands.[63, 96, 178] This was accompanied by a considerable narrowing of absorption and fluorescence bands and their structuring (Fig. 3), and also in the increase in the quantum yields of fluorescence by several orders of magnitude.[96, 110, 178] This was explained by fact that the structure of a merocyanine with positive solvatochromism approached that of ideal polymethine **A2** due to the strengthening of electrostatic interactions with the solvent in the ground state as a result of more ordered solvation shells at low temperatures.

Studies on the thermochromism of dye **39c** with negative solvatochromism have shown [179] that a decrease in the temperature of its ethanolic solution down to 77 K was accompanied by a substantial broadening of its absorption and fluorescence bands rather than their narrowing and also by their hypsochromic shift (Fig. 4).[179] This was associated with stronger polarity of merocyanine **39c** in the ground state, *i.e.*, its closeness to the **A3** structure.

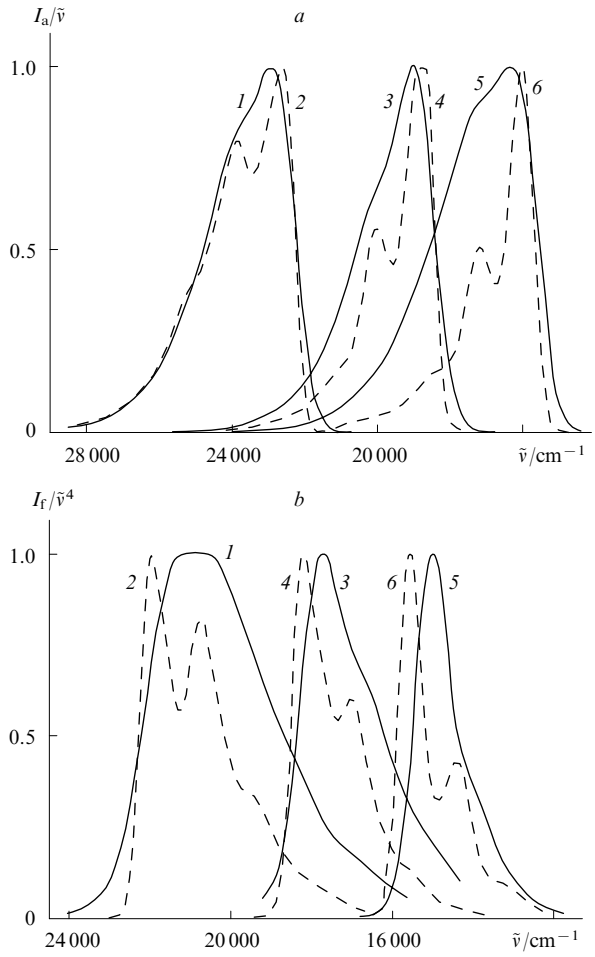


Figure 3. Normalised absorption (*a*) and fluorescence (*b*) spectra of merocyanines **39a** (*1*, *2*), **39b** (*3*, *4*) and **39c** (*5*, *6*) in ethanol at 293 (*1*, *3*, *5*) and 77 K (*2*, *4*, *6*).[178]

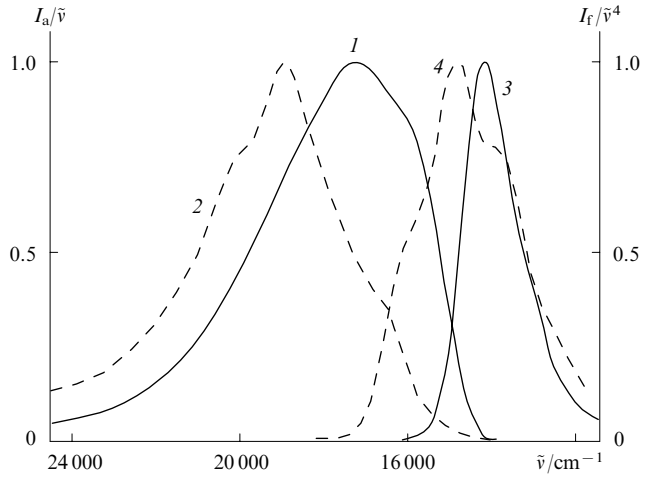
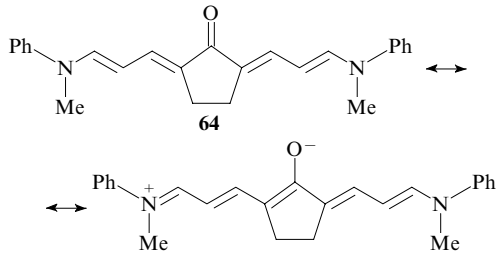


Figure 4. Normalised absorption (*1*, *2*) and fluorescence (*3*, *4*) spectra of dyes **49c** in ethanol at 293 (*1*, *3*) and 77 K (*2*, *4*).[179]

4. Studies of merocyanines by the methods of quantum chemistry, X-ray diffraction analysis and NMR spectroscopy

Due to the fast development of computer technologies and the progress in computation techniques, the quantum chemical calculations now represent not only an available method but also necessary one for solving the wide spectrum of theoretical and applied problems of chemical science. The application of quantum chemical methods to merocycanines as to other compounds with a well-developed system of conjugated π-bonds is useful not only in studying their properties, but also in verifying the calculation methods themselves, because such objects still present certain difficulties for calculation.

Insofar as a solvent may considerably affect the structure and properties of merocyanines, it is not surprising that the largest number of studies in this field are asociated to one extent or another with approaches towards adequate consideration of solvation effects.[46, 88, 91, 96, 108, 118, 130, 131, 180–195] The large volume of performed studies substantially improved the agreement between theoretical models of merocyanine solvatochromism and the experimental results. For example, Ponterini and co-workers [108] assessed the applicability of the solvatone model CS INDO to the description of solvatochromism and solvatofluorochromism of merocyanines. Two dyes were studied that exhibited solvatation effects of the opposite signs, namely, the classical Brooker stilbazolium merocycanine (**57**) (a traditional subject of such studies [118, 130, 131, 180]) and ketocyanine **64**, which exhibits the clearly pronounced positive solvatochromism (and solvatofluorochromism).



64

For these compounds, the solvatochromic shifts for the vertical transition from the ground state to the first Frank–Condon state $S_1^{FC} \leftarrow S_0$, and also for the $S_1 \rightarrow S_0^{FC}$ transition were theoretically calculated. To estimate the medium polarity, the following function of dielectric permittivity was chosen: [108]

$$k(\varepsilon) = \frac{\sqrt{\varepsilon} - 1}{\sqrt{\varepsilon}},$$

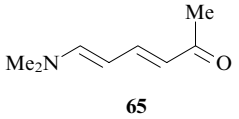
i.e., the specific solvation was totally ignored, although both subjects of studies were, for example, capable of forming hydrogen bonds with proton-donating solvents. In calculations of the equilibrium geometries of the ground and the first excited states, the effect of the medium was also totally ignored. However, even this simplified model for the calculation of the absorption and fluorescence solvatochromic shifts produced the results adequately consistent with the experiment. The best correlation with the experimental data was achieved for ketocyanine **64**, which exhibited positive solvatochromism. For merocyanine **57** characterised by reverse solvatochromism, the calculated shifts were underrated. Probably, this can be explained by the larger effect of solvation on the structure of a more polar dye. In both cases, the results for proton-donor solvents were entirely inadequate.

Naturally, such calculations are too laborious, and the medium polarity was often modelled by simpler methods, for example, by using a 'sparkle', *i.e.*, a model positive or negative ion with zero polarisability.[184, 194]

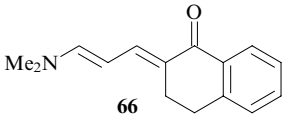
No studies that would adequately calculate the vinylogue series of merocyanines were found. The calculated maxima and vinylene shifts in the absorption spectra for such series were far underestimated as compared with experimental results.[7] On the other hand, such calculations also gave inadequate results for symmetrical polymethine dyes.

The quantum chemical calculations for dyes with negative solvatochromism for which the semi-empirical and *ab initio* calculation methods predicted a decrease in the dipole moment in the excited state rather than its increase still pose an important problem. By the example of the Brooker merocyanine (**57**), it was shown [108] that account of the solvent polarity in quantum chemical calculations can lead to the lower dipole moment in the excitation as compared with vacuum. However, there is another viewpoint according to which the calculation methods themselves should be improved to be applied to merocyanines; this has been performed, *e.g.*, in Ref. 118.

Yet another problem is associated with the calculation of the relative position of $^1(\pi_H\pi_L^*)$ and $^1(n\pi_L^*)$ states of merocyanines, because this substantially affects their fluorescence properties. If these states are close in energies, the interaction of their vibronic sublevels strengthens the internal conversion, which leads to the non-radiative deactivation of the $^1(\pi_H\pi_L*)$ fluorescence state and the reduction of the quantum yield of fluorescence.[196] It was shown [160] that for simple merocyanines **65** and **66** the low $^1(n\pi_L^*)$ state substantially reduced their quantum yields of fluorescence.



65

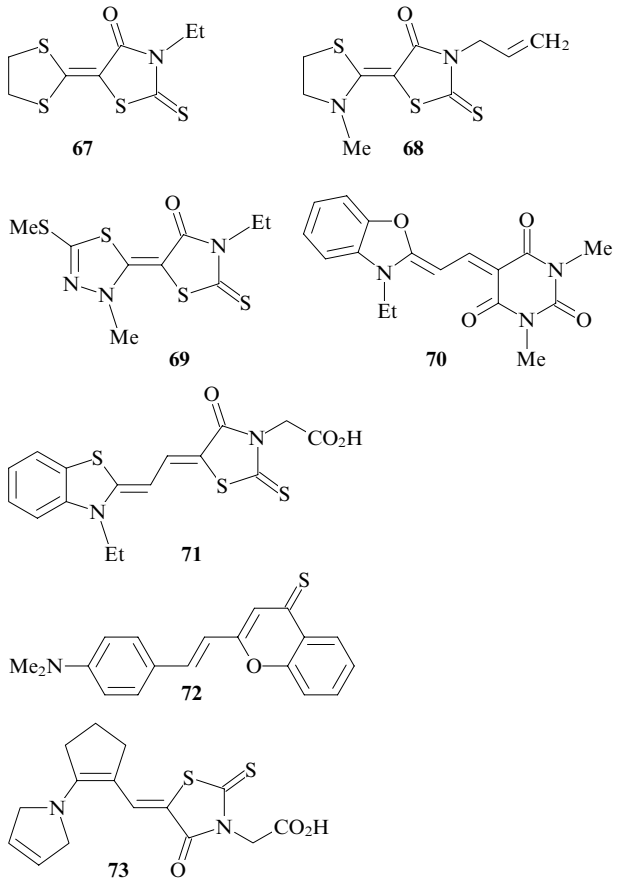


66

The increase in the medium polarity lowered the energy of $^1(\pi_H\pi_L^*)$ state to the greater extent than the energy of $^1(n\pi_L^*)$ state, because the former state was more polar. For example, for compound **65** in ethanol $^1(\pi_H\pi_L^*)$ became the S_1-state and the quantum yield of fluorescence for this dye increased by more than one order of magnitude as compared with its solution in toluene. It was noted [160] that this factor is probably less important for more complex dyes. Indeed, by the example of a series of merocyanines that contained a malononitrile or *N*,*N*-diethylbarbituric acid moiety, it was shown [107] that the experimental values of Φ_f did not agree in the least with the calculated position of $^1(\pi_H\pi_L^*)$ and $^1(n\pi_L^*)$ states.

X-Ray diffraction analysis can provide more objective information on the spatial and, hence, electronic structure of merocyanines. X-Ray diffraction data are a good reference point for quantum chemical calculation methods. They provide the absolute proof (or disproof) of the results obtained using different experimental methods. However, few studies of merocyanines in this direction were largely of the descriptive, structural character [7, 44, 85, 98, 197–202] and, in addition to structures of dyes **34**, **35**, **57**, **62**, considered the

structures of zero- or dimethinemerocyanines (for example, compounds **67**–**73**).



A comparison of X-ray diffraction data with the results of quantum-chemical calculations has revealed [108] considerable deviations between them, namely, for compound **57**, calculations predicted the alternation of bond lengths, which corresponds to a structure in the range of **A1**–**A2**, whereas experimental data showed that its structure approached that of bipolar polyene **A3**. This was explained by the fact that dye **57** is crystallised together with three water molecules and the latter strengthen the polarity of dye molecules, being coordinated on the oxygen atom of the carbonyl group. Another possible explanation stems from the imperfect calculation method.

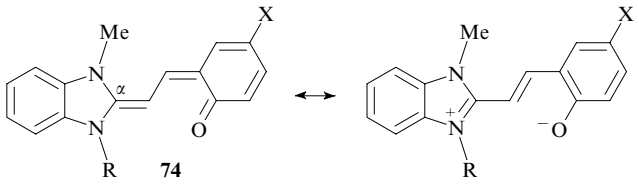
X-Ray diffraction was virtually never applied to merocyanine series. Two vinylogues (**39a** and **39c**) were studied,[202] which made it possible to prove that with the PC elongation, the structure approached that of neutral polyene **A1,** as was predicted based on the experimental electronic absorption spectra and quantum chemical calculations of the BLA parameter. However, dyes **39a**–**c** exhibited positive solvatochromism, *i.e.*, for them, the quantum chemistry methods worked adequately albeit on the qualitative level. Thus, it is interesting to elucidate the structures of a merocyanine series characterised by negative solvatocromism and, hence, by the reverse alternation of PC bond lengths.

The distribution of charges and bond orders in a merocyanine chromophore can be studied using NMR spectroscopy.[46–48, 52, 102, 148, 151, 170, 203–212] The majority of studies in this direction were carried out more than 20 years ago. The most important among them were the publications [203–208] devoted to the comprehensive investigation of NMR spectra and the electronic structure of the simplest streptocyanines **1a** ($n = 1-5$, R = Me).

In these studies, it was concluded that the alternation of spin–spin coupling constants of protons in a PC corresponds to the alternation of the bond orders in a chromophore.[203, 207] The levelling of spin–spin coupling constants for a chain (structure **A2**) was achieved in a low-polar chloroform. On going to polar solvents (CD_3OD, D_2O), the alternation of bonds was observed; moreover, this corresponded to the electronic structure of a bipolar polyene **A3**, in agreement with the negative solvatochromism of the subjects of study. The analysis of chemical shifts of ^1H and ^{13}C nuclei in PC allowed the NMR spectral signals to be correlated with the charges on carbon atoms calculated by a quantum chemical method (the Pariser–Parr–Pople method). The relationship between the solvent polarity and the amplitude of alternation of shifts of neighbouring carbon atoms in PC was revealed. Furthermore, ^{15}N NMR spectra of streptocyanines **1a** were studied for a series of solvents with widely differing polarity.[206] It was shown that an increase in the solvent polarity shifted the corresponding signal of the ^{15}N nucleus to the weak field, which pointed to the increase in the polarity of the dye electronic structure.

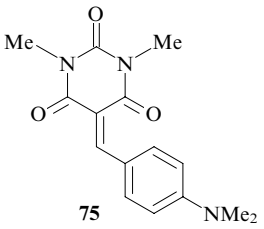
NMR spectra of vinylogous series of merocyanines **39a**–**c**, **41a**–**c**, **51a**–**c** and **53a**–**c** with the positive and negative solvatochromism were analysed.[52, 102] This made it possible to follow the effect of both the PC length and the donor–acceptor properties of terminal groups on their NMR spectra. It was found that ^1H and ^{13}C NMR spectroscopy can serve as a tool for studying the transition between the polyene and polymethine states of merocyanines with the positive and negative solvatochromism. Reference atoms were proposed the signals of which in the ^{13}C NMR spectrum were most sensitive with respect to changes in the symmetry of the merocyanine electronic structure. It was shown that the chemical shifts of PC atoms correlate well with the charges on the corresponding atoms found by quantum chemical calculations.

Using ^{13}C NMR spectroscopy, the effect of different substituents in the acceptor (oxyphenyl) moiety of dyes **74** on their electronic structure was studied.[209]

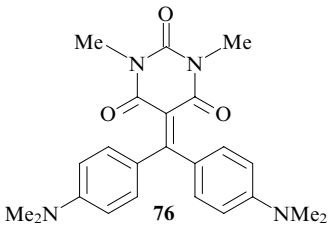


qIt was shown that the electron-donating substituents X enhanced the alternation of chemical shifts of chain atoms by shifting the α-atom signal to the upper field, and also gave rise to the bathochromic shift of the long-wavelength electron transition. The elucidated PC geometry in molecule **74** was confirmed by NMR spectroscopy. This study was carried out with the fixed PC length and only one solvent.

The ^{13}C NMR spectra of merocyanines **75** and **76**, *i.e.*, the barbituric acid derivatives, were studied.[204] The obtained results were used in the interpretation of structural deviations of these compounds and their solvatochromism.



75



76

5. Aggregation of merocyanines

Self-aggregation and aggregation of organic molecules were the subject of studies in actively developed areas, namely, supramolecular chemistry and nanochemistry.[213,214] This phenomenon is common for cyanine dyes, because it is the perculiarities of their structure, namely, the considerable dipole moments, the alternation of opposite signs and the planar structure of the chromophore, that determined the high energy of intermolecular interactions.[11]

Aggregation is less typical of merocyanines as compared with the corresponding cationic polymethines. It was often achieved by special methods aimed at strengthening the intermolecular interactions. For example, by incorporating functional groups capable of carrying a negative charge (carboxyl or sulfo groups) or alkyl susbtituents into the molecular structure, carrying out association in the liquid–crystal phase or in the presence of metal salts.[215–221] The aggregation proceeded most easily in media where the dye solubility is insignificant (in water, n-hexane), or on the surface of certain supports, for example, silver halides and d-metal oxides.[213,222]

Classification of supramolecular entities was carried out based on their spectra by comparing them with the spectra of their monomeric forms. It is common practice to distinguish J-aggregates, which are characterised by bathochromic shift, sharp narrowing of the absorption band and its resonance coincidence with the fluorescence band,[59,223–232] and H-aggregates, which are characterised by bathochromic shift and quenching of fluorescence.[223,233] The first type of aggregates predominated in photoemulsions.[4,223] The relationship between the structure of aggregates and their spectra was described in terms of the exciton theory of oscillator coupling.[234]

The most thoroughly studied type were J-aggregates, particularly, their absorption spectra were studied as a function of the number of molecules in the aggregate.[207,235] One of the main reasons for such interest was associated with the exceptionally high intensity and the small width of their absorption bands, which is important for non-linear optics, laser radiation modulation, *etc*.

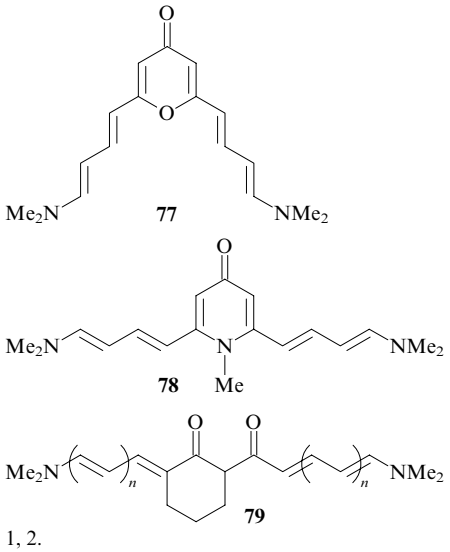
Keen attention was drawn to the supramolecular aggregates of merocyanines formed at interfaces, particularly, the ordered Langmuir–Blodgett films[220,236–248] and also to aggregates of dyes on inorganic supports.[249–252]

Bis-dyes that include two chromophores connected by a rigid or flexible bridge (spacer) are the ideal models for studying aggregation. The spectral properties of bismerocyanines were studied in comparison with the corresponding original 'mono-dyes'.[47,63–65] The observed spectral effects were explained within the framework of the exciton theory of oscillator coupling.[234]

Thus by the example of compounds **26** and **28**, it was found that solvatochromism is stronger manifested for bismerocyanines as compared with monomeric dyes.[63,64] This effect was explained by the interaction of charges of closely located chromophores of bis-dyes in both their ground and excited states. It was shown that the degree of interaction of chromophores connected in the non-rigid manner depends on the spacer length (for compounds **28**), and also on the solvent polarity.[64] Obviously, the manifestation of solvatochromism for dye **26** depends on the possibility of its existence in both *syn*- and *anti*-conformations, where, according to NMR studies,[63] the ratio of conformers depends on the medium polarity (polar solvents increased the content of the *syn*-conformer). According to the theory,[234] the *syn*-conformer does not fluoresce, in contrast to its *anti*-form.

By the example of compound **27** in which chromophores are connected by a sufficiently rigid tris-n-dodecyloxy)-*m*-xylylene spacer, the trend of bismerocyanines towards the formation of supramolecular aggregates was studied.[65] It was shown that a bis-dye is more prone to the formation of aggregates of the J- and H-types as compared with the corresponding original 'mono-dye'. These results agree with the results of studying cationic polymethine dyes.[11]

The important classes of bis-dyes of the merocyanine type, namely, ketocyanines and diketocyanines, were studied in detail.[31–35,210–212,253] Most of them involved the cross-conjugated chromophore systems (see structures **12**, **13**, **77**, **78**); however, diketocyanines with non-conjugated chromophores were synthesised,[31] *e.g*., compound **79**.



77 **78** **79**

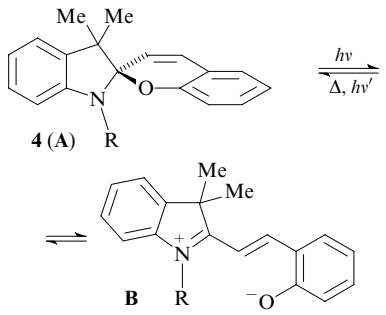
$n = 1, 2$.

For compounds **77** and **78**, using a wide set of methods (electronic spectroscopy, ^{1}H NMR spectroscopy (gNOESY method), quantum chemical calculations), it was proved[212] that the molecular conformations shown above are preferential. Due to the sharp angle between the chromophores in molecule **77**, its electronic absorption spectrum included two bands in the visible spectral region, where the short wavelength band was more intense. And *vice versa*, for dye **78**, the angle between chromophores was close to 180°, and its electronic spectrum included only one band in the visible range (the second, short-wavelength transition was forbidden).

6. Spiropyrans

An important type of merocyanines are spiropyrans, a class of compounds actively studied over the last 20 years.[5,29,58,146,193,242,243,254–265] Due to their remarkable ability to reversibly pass from their colourless spiroform to the coloured merocyanine form, they find

application in non-linear optics, modern optical information carriers, molecular-scale logical switches and other nanodevices.[254, 255, 266, 267]



The transition between forms **A** and **B** of these compounds proceeds reversibly by the photochemical and thermal mechanisms, and also under the action of chemical reagents (protons, metal ions).[268, 269] Thus, their chemical structure and spectral properties can be controlled using some external tool, *e.g.*, illumination with a definite wavelength.

An important problem of chemistry of spiropyrans is the increase in their photostability. The simplest way to achieve this is the pass to spiroxazines, which are more resistant to light.[270]

Studying the spectral characteristics of spiropyrans has shown that in their open form, almost all of them exhibited negative solvatochromism.[5, 255] Quantum yields of fluorescence were very small at ambient temperatures but, as for common merocyanines,[178] increased by orders of magnitude when ethanolic solutions were cooled to 77 K (solvent in the glassy state).[268]

Spiropyrans were convenient subjects for studying the photophysical properties of merocyanines, first of all, the processes of their photoisomerisation and excited-state relaxation.[254, 268] By their example, it was shown [254, 268, 269] that substituents in end groups of merocyanines have a substantial effect on their photophysical properties, particularly, the photoisomerisation processes. For example, the introduction of a nitro group into the benzene ring of structure **4** substantially increased the yield of the triplet state the formation of which often precedes the *cis–trans*-isomerisation, *i.e.*, the transition between the closed and open forms.[271–274] Raman spectroscopic studies of the structure of aggregates formed by open spiropyrans have shown [270] that the 6-NO_2 group stabilises this structure due to its electrostatic interaction with the positively charged nitrogen atom of the heterocyclic moiety of the neighbouring molecule.

IV. Practical application of merocyanine dyes

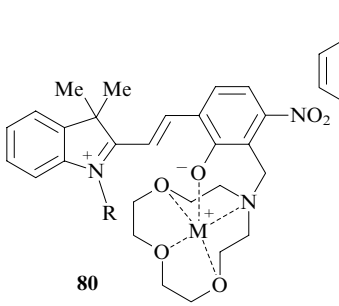
1. Merocyanines as probes and markers in chemical analysis, biology and medicine

The spectral, particularly, fluorescence properties of merocyanines strongly depend on the environment characteristics, namely, its polarity, viscosity (and microviscosity), the presence of different reagents capable of formation of complexes or associates with dye molecules. Due to these properties, merocyanines were among the first reference points used in building the scales of solvent polarity,[121] for determination of water content in organic solvents and have also found their application as the sensors, probes and markers in the chemical analysis, especially, in biomedicinal studies.[26, 30, 119, 187, 275–305]

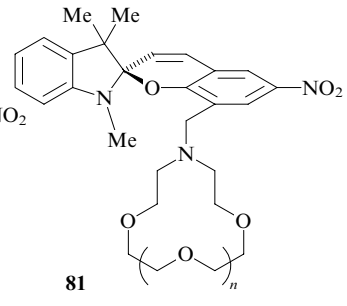
In molecular biology, merocyanines were used as fluorescent probes for the determination of gradients of polarity of biological media, intracellular pH, microviscosity of membranes and biopolymers,[261, 306] as the tags (markers) of specific biological sites.[26, 187, 300, 307–309] These studies preferentially used dye MC-540 or its analogues.[119, 275, 278, 281, 285–288, 291–296, 298]

A large series of metallochromic compounds are known, the spectral properties of which substantially depend on the microconcentration of metal ions. A considerable part of them consists of merocyanines [29, 59, 254, 257, 259, 263, 310–317] mostly of the spiropyran type.

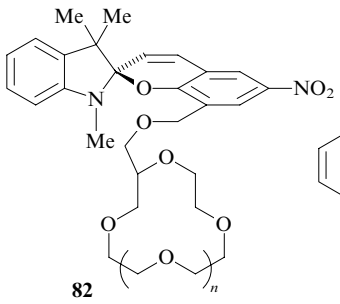
The pronounced negative metallochromism of the merocyanine form of spirocompounds [29, 59, 254, 263] was associated with the possibility for a metal cation to coordinate the oxygen atom of oxyphenyl residue that carries a considerable negative charge (compound **80**). This effect was enhanced by the introduction of metal ions into coordination spheres (dyes **81**–**83**), most often these were crown- and azacrown groups.[254, 312, 317]

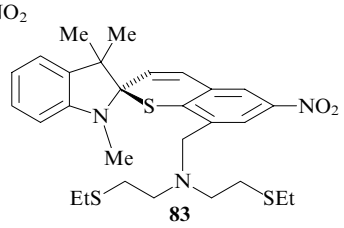


R = Me, n-$C_{18}H_{37}$.



n = 1–3.

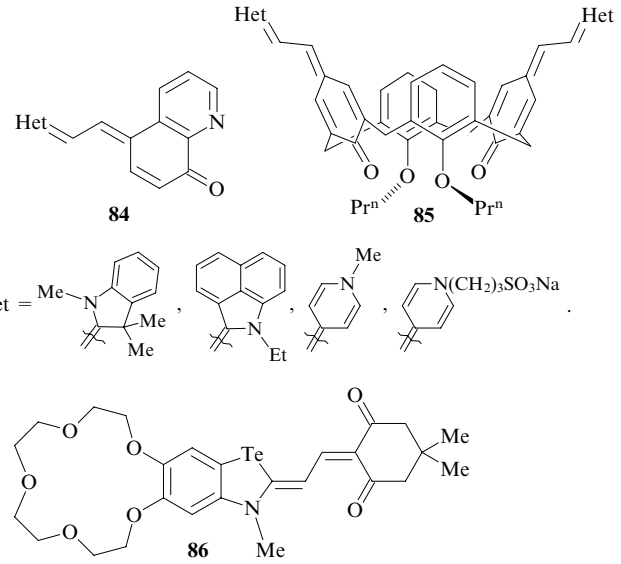




n = 1–3.

Such compounds exhibited not only the high sensitivity with respect to insignificant amounts of metal ions (10^{-5}–10^{-6} mol litre^{-1}) but also, quite often, the high selectivity. Moreover, using such spirocompounds, it was possible not only to determine but also regulate the microconcentrations of ions in solutions,[254] because the stability constants of complexes substantially differ for their open and closed forms.

Other types of metallochromic merocyanines are known,[254] for example, 8-hydroxyquinoline derivatives (**84**),[314] calixarenes that include an oxystyryl fragment (**85**),[59] and also various structures containing a crown macrocycle,[312, 318, 319] for example, dye **86**. Most of them, in contrast to spiropyrans, exhibited positive metallochromism.



The listed metallochromic merocyanines differed from spiro compounds in higher photostability, the existence of only one form (which gives certain advantages for the analysis), and wider potentials for structural modifications.

Spiro compounds have found application as the regulators of DNA hybridisation.[320] For this purpose, oligonucleotides containing a covalently bound spiropyran residue were synthesised. A merocyanine capable of acting as a molecular 'engine' of transmembrane transport was described.[290]

Together with organic dyes of other classes, merocyanines were actively studied as the potential sensitisers for photodynamic therapy of cancer.[5, 282, 321] The leadership in this field is still held by phthalocyanines for which the mechanisms of transport and localisation were studied in most details.[322, 323] Among merocyanines, the most promising is the dye MC-540 (**60**) and its benzothiazole analogues. Due to their high selectivity with respect to tumour cells, they were widely studied as the antileukemic drugs and also as the probes for detecting this disease in early stages.[170, 283, 287, 289, 324] The mechanism of their action is the same as for porphyrins and phthalocyanines, *i.e.*, the sensitation of the singlet oxygen formation.[325] This followed from the studies of the processes of self-oxidation and *cis*–*trans*-isomerisation of the dyes mentioned and also from the fact of the high efficiency of selenium-containing analogues for which the quantum yields of their transition to the triplet state was the maximum, as for phthalocyanines. A similar mechanism was typical of certain merocyanines that proved to be promising antimicrobial agents.[299]

2. The use of merocyanines in non-linear optics

The development of quantum light generators (lasers) gave rise to a new branch of physics, non-linear optics. Studies in this field were directed to the development of highly effective materials for the second harmonics generation to be used in electrooptics. For several decades, keen attention was drawn to the search and development of materials that exhibit non-linear optical (NLO) and electrooptical properties [255, 326–344] and are capable of competing with conventional NLO-media, inorganic crystals.[345] The main parameter of this quest was high hyperpolarisability (β_0) typical of molecules the electronic excitation of which is accompanied by a considerable intramolecular charge transfer.

For the donor-and-acceptor substituted 'one-dimensional' chromophores, the β_0 value can be assessed from the variations of the molecular dipole moment ($\Delta\mu$) in the excitation.[96, 327, 346]

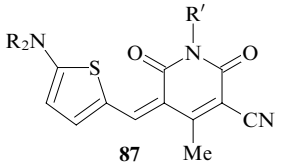
$$\beta_0 = \frac{6\mu_{ag}^2\Delta\mu\lambda_{ag}^2}{(hc)^2} = \frac{3e^2\hbar^2}{2m}\,\frac{W}{\left[W^2-(2\hbar\omega)^2\right]\left[W^2-(\hbar\omega)^2\right]}\,f_e\Delta\mu,$$

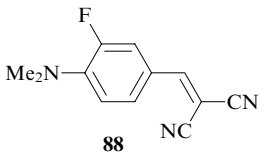
where μ_{ag} is the transition moment, λ_{ag} is the transition wavelength, h is the Plank constant, c is the velocity of light in vacuum, e is the electron charge, $\hbar$ is the normalised Plank constant, m is the electron mass, W is the energy difference between the ground and first excited states of a chromophore, ω is the main frequency of laser radiation, f_e is the transition oscillator strength,

$$\Delta\mu = \mu^{FC} - \mu_g$$

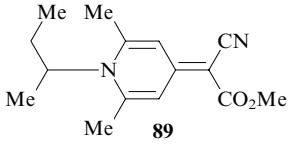
is the difference between dipole moments of the Frank–Condon and ground states. Hence, to develop highly effective materials for non-linear optics, deeply coloured compounds are required the molecules of which have the dipole moments that substantially differ in the ground and excited states.

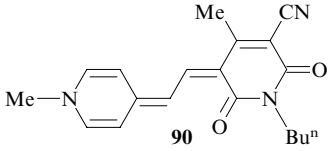
Due to the high $\Delta\mu$, merocyanines even at low concentrations can substantially change the refraction index of the medium (polymer). This property has found its practical application in the development of photorefractive materials used in modern information technologies and in holography.[255, 347–349] For the successive use, such compositions should exhibit photoconductivity, high optical parameters and photostability. These properties were achieved by adding of an electroactive chromophore with a high coefficient β_0, a sensitiser and a strong acceptor, *e.g.*, 9-dicyanomethylidene-2,4,7-trinitrofluorene, to the light-conducting organic materials (polyvinylcarbazole, triarylamines).[138] Merocyanines (for example, compounds **87**–**92**) are well suited to the first two requirements.

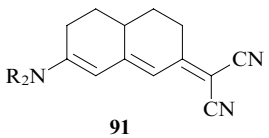


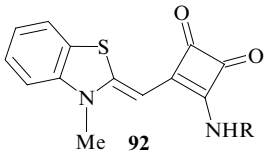


R = Alk; R–R = $(CH_2)_n$ (n = 4, 5), $(CH_2)_2O(CH_2)_2$; R′ = Alk.









R = Alk; R–R = $(CH_2)_n$ (n = 4, 5), $(CH_2)_2O(CH_2)_2$.

R = Alk.

The possibilities of using different supramolecular formations (J- and H-aggregates, ordered Langmuir–Blodgett films) of merocyanine dyes that can exhibit NLO properties substantially different from the properties of non-associated dyes were actively studied. Such nanoformations have already found their application in quantum electronics and other fields of modern technology.[350–353]

Characteristics of modern lasers, first of all, the high power density of pulsed radiation, allowed the two-photon excitation to be carried out sufficiently easily in different media. In connection with this, technologies based on two-photon absorption (TPA) were actively developed. Recently, the multi-photon confocal fluorescence microscopy and the production of 3D microstructures were also actively developed; the bulk (3D) optical memory and photodynamic therapy with two-photon excitation showed great promise.[354–356]

The successful development of TPA-based technologies requires, besides the corresponding excitation sources, the substances with a large two-photon absorption cross-section. In recent years, several classes of such compounds, namely, substituted fluorenes, porphyrins, pyridines, *etc*., were found and studied.[357] The greatest promise for two-photon laser technologies was demonstrated by merocyanines, for example, DCM (**62**).[143, 356, 358, 359]

The first studies devoted to the two-photon-excited fluorescence of merocyanines **39b**,**c**, **41c**, **47c** and **49c** and the determination of TPA cross-section of these dyes are documented.[360, 361] It is noteworthy that in certain cases the cross-section exceeded that of a classical luminophore, rhodamine 6G, by more than an order of magnitude. It was assumed that at the excitation power density higher than 100 MW cm^{-2}, three-photon absorption was also observed in addition to TPA.

It was found that merocyanines (for example, compounds **39c**, **41c**, **47c**, **49c**, **62**) are promising active laser media that generate radiation with high efficiency and large Stokes shifts.[359–362] This can be explained as follows. First, irrespective of the solvatochromism type, the electronic structure of their fluorescence state approaches the state of ideal polymethine **A2**. This increases the quantum yield of fluorescence and hence the efficiency of its generation. Second, the possibility that structure **A2** shifts to both structure **A1** (merocyanines with positive solvatochromism) and **A3** (merocyanines with negative solvatochromism) in its ground state causes the broadening of the absorption band and increases the Stokes shifts of merocyanines. The mentioned factors enhanced the efficiency of generation, the former, due to the larger absorption cross-section at the wavelength of 532 nm and the latter, as a result of a decrease in the superposition of absorption and fluorescence bands.[361]

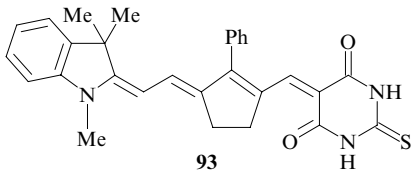
3. Merocyanines as organic semiconductors

Currently, the molecular photosemiconducting systems have become the object of active theoretical and applied studies.[138] Attention drawn to such systems was explained by the fact that they may help to realise the high-rate processing and recording of information. Among such molecules, attention was focused on merocyanine dyes with the unique set of photophysical and photochemical properties.[138, 363–367]

The improvement of existing photoelements and the development of new effective types for solar power production that can operate in a wide spectral range were among the most important problems of modern science.[363, 368] Due to the bipolar structure of merocyanines, their use is very promising in solar energy converters, because they are capable of photogeneration of opposite-sign charge carriers.[138] The high photoconductivity of materials based on merocyanines was achieved due to the fact that during the light generation, both holes and electrons are mobile while their recombination in dye molecules is hindered. Moreover, for merocyanines, the higher photoconductivity was also caused by the fact that mobile charge carriers are separated and move away from one another, whereas for ionic dyes, the counter-ion effectively holds the photogenerated charge carrier.

The photoconductivity of poly(*N*-epoxypropylcarbazole) (PEPC) films with additions of merocyanine dyes was found to increase as their degree of solvatochromism increased.[369, 370] The greatest effect was achieved for merocyanines with positive solvatochromism and the smallest effect corresponded to negative solvatochromism. It was shown that the more pronounced bipolar structure of the excited state of the former (as compared with the latter) increased the probability of the electron capture from a PEPC molecule by the dye to form a carbazole radical cation that provides p-conduction of the polymer.

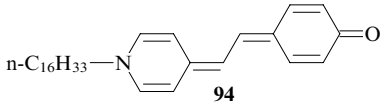
Aimed at the development of new materials exhibiting photoconduction in the near IR spectral range, polymeric compositions that contained merocyanines **54c** and **93** as the sensitisers were prepared.[371, 372] The dyes absorbed light in the near IR range and their electronic structure approached **A2**. Hence they demonstrated a narrow intense absorption band in the mentioned range. In its spectral characteristics, merocyanine **93** approached the corresponding symmetric cationic tricarbocyanine with two terminal indole moieties,[371] but, as a sensitiser for organic photosemiconductors, lacked the drawbacks of the latter, first of all, those associated with the dark conduction currents typical of ionic dyes.[138]



93

Merocyanines were used as the components of the photoelement active media,[138, 373, 374] but, more often, as the sensitisers that extended the sensitivity range of other materials used in photoelements, for example, TiO_2.[24, 375–390]

Thermoelements using merocyanines as the working materials,[391] for example, dye **94**, are known.



94

Being heated to 65 °C, such an element produced current at the voltage of up to 310 mV.

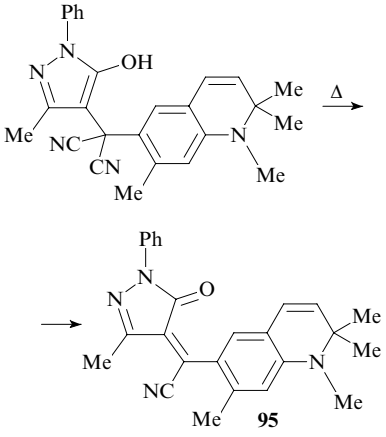
The sensitising properties of merocyanines have found their application in electrochemistry and photocatalysis. Sensitisation of semiconducting porous electrodes (TiO_2, In_2O_3) substantially changed their potential, which made it possible to carry out, *e.g*., water electrolysis, at a lower voltage.[145, 251, 392, 393]

In the future, electroluminescence properties of merocyanines, caused by the ability of their molecules to both donate and withdraw an electron to form radical cations and anions, respectively, may found their application.[111, 120, 394] Based on the studies of the photoluminescence and voltammetric characteristics of merocyanine films, their electroluminescence properties were explained by the recombination of oppositely charged radical ions.

The processes of formation and subsequent recombination of electron – hole pairs in polymeric films lie in the basis of holographic detecting media (HDM). As the HDM detection sites, charge-transfer systems were used in which the electron-donating and -withdrawing molecules (or their fragments) either formed together the adduct or were chemically bound by insulating polymethylene groups or a system of conjugated π-bonds.[138] Merocyanines belong to the latter HDM type. Holographic detecting media based on merocyanines are used in recording holograms by the photothermoplastic method; merocyanines have a narrow intense spectral band and the high holographic sensitivity; this is why they should be preferred as the photogeneration sites for HDM over the intra- and intermolecular charge-transfer complexes. The considerable intensity and selectivity of optical absorption in the visible spectral range (for example, for merocyanine **39c**) ensures the high holographic sensitivity and requires no special measures for the HDM protection from the external light.[395] Photophysical properties of such HDM are independent of the film preparation conditions, and a latent electrostatic image is formed at the exposure even without their preliminary charging in the corona discharge. This allowed the high optical uniformity of HDM to be achieved, whereas the transmission characteristics, the signal/noise ratio and the cyclicity of HDM operation were determined by the thermoplastic and rheological properties of the polymeric matrix.[138]

4. Miscellaneous application fields of merocyanines

The dependence of the electronic spectra of merocyanines on the temperature has also found practical application. Certain thermochromes were used for protection of securities,[262] in thermoprinting and other thermographic processes. Here, sometimes, it is thermoinitiation of chemical reactions that was used rather than thermochromism as such. In this case, substantially strict requirements were imposed, namely, 1) high rate of precursor transformation to the dye, 2) possibility of mechanical or chemical initiation; 3) resistance to discolouration. This problem was considered in sufficient detail.[396] Thus the following transformation was used for thermoprinting:



95

The uncoloured precursor eliminated an HCN molecule to become a yellow dye.

Several papers were devoted to studies of the merocyanine-induced photopolymerisation.[397 – 399]

Up to recently, merocyanines were known first of all as solvatochromic compounds. However, it was found[369, 400] that long-wavelength electronic absorption bands of merocyanines are sensitive with respect to the external electric field, *i.e.*, these dyes exhibit electrochromism. Moreover, the bands were shifted in opposite directions for merocyanines with opposite-sign solvatochromism. The electrochromism was caused by variations in the contributions of the bipolar and neutral limiting structures to the ground and excited states, *i.e.*, associated with the intramolecular charge redistribution upon the application of an electric field. However, due to the bipolarity of merocyanines, this could also be caused by the variable orientation of their molecules in the electric field.[401] It should be noted that the possibility of controlling the optical properties of merocyanines by an external electric field opens up new application fields for these dyes.

V. Conclusion

The progress in synthetic chemistry of merocycanines will be related to the elaboration of new synthetic methods and the production of compounds with desired properties. The integration of a merocyanine moiety and other functional group in one molecule appears to be promising, because, as was already shown, such compounds exhibit new valuable properties.

Merocyanines with relatively long polymethine chains attract special interest of scientists. Studying polyene – polymethine transitions in these compounds should provide additional information on such important problem as the theory of chromaticity. This is explained by the fact that the uniform distribution of electron density in the chromophore of symmetrical dyes is violated when their PC become considerably longer.[402] This effect, the so-called collapse of symmetry, has found its explanation in several quantum chemical calculations.[403] On the other hand, merocyanine molecules are *a priori* non-symmetric; and, hence, such symmetry degeneration should not occur and, from the theoretical standpoint, the attainment of the ideal polymethine state **A2** is possible for merocyanines with sufficiently long PC as well. However, modelling of such a molecule should take into account the fact that with the PC elongation, the contribution of the non-polar polyene structure **A1** considerably increases. Hence, to reach the 'cyanine limit' for long-chain merocyanines, the end groups with pronounced donor-acceptor properties should by chosen. The attention to long-chain merocyanines was also associated with the possibility of synthesising new compounds with strong solvatochromism that would exhibit much higher intensity of spectral bands as compared with Reichardt's betaine.

Merocyanines with long PC also attract attention as deeply coloured dyes capable of intense light absorption in the near IR spectral range that corresponds to the working range of the most important optoelectronic devices. The development of such dyes is important for modernisation of solar cells, because by selecting a matching merocyanine it is possible not only to achieve the conduction type necessary for the photovoltaic effect, but also to obtain effective absorption in the solar spectrum maximum.

Up to now, the electron absorption and luminescence spectroscopies were the main methods of studying the electronic state of merocyanines. These studies were carried out in solutions, and the electronic state of dyes could substantially vary in the solvent field.[7] It is difficult to obtain reliable electronic spectra in the solid state due to the deformation of spectra as a result of electron level splitting under strong intermolecular interaction in a crystal. IR spectra lack these drawbacks. However, they provide little information due to the close vibrational frequencies of C=C, C=N, C=O bonds in the main chromophore moieties of the majority of merocyanines. The spatial structure of dye molecules in a crystal can also be deformed in the crystal field. The transition of merocyanines into the gas phase is hindered. The high sublimation temperature leads to either the dye decomposition or the thermochromic effects (the shift of spectral bands or changes in their form and intensity). It is possible to avoid undesired side processes by recording spectra of cooled molecules in vapour using the supersonic jet method.[404–406] This method can provide qualitatively new information on the electronic structure of the ground and excited stated of merocyanines, the nature of intermolecular interactions when going from gas to solution, the channels of deactivation of electron-excited states. Unfortunately, this method was never used for merocyanines so far.

Considering quantum chemical calculations of merocyanine molecules, it is evident that their progress was associated with the wide use of *ab initio* calculation methods and also with the adequate modelling of the solvation shell, which, in principle, can be achieved by using modern compute clusters.

Bearing in mind the wide diversity of practical applications of merocyanines and also the uniqueness of their luminescence-spectral, non-linear-optical and electrophysical properties, it can be assumed that the latter can become promising components of the modern nanocomposite and hybrid materials.[407] At present, the growning interest in the use of merocyanines in alternative power sources and the extension of their application field in different NLO technologies deserve mention.

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