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The Conformations of Polymethine Dyes

A.M.Kolesnikov and F.A.Mikhailenko

The conformational features of polymethine dyes and related compounds are examined and the principal factors controlled by the conformational equilibrium are identified. The methods for the determination of the geometrical structures of polymethines are discussed. Special attention is devoted to a new method for the determination of their conformations—from the absorption spectra of dyes with two chromophores.
The bibliography includes 140 references.

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I. INTRODUCTION

Polymethine dyes are a special class of organic compounds: they possess the unique ability to sensitise to visible light light-sensitive materials based on silver halides. The capacity of polymethine dyes for aggregation and adsorption on silver halides depends greatly on the steric structure of the cations of the dye itself.[1-3] In particular *cis–trans* isomerism has a pronounced and a by no means unambiguous influence on the effectiveness of the sensitisation.

Yet another field in which polymethine dyes are applied has been established in recent years—laser technology. Lasers based on these compounds generate radiation in the range 500–1250 nm. It has been established that the isomerisation of polymethine dyes plays an important role in the degradation of the photoexcitation energy, which ultimately affects the luminescence and generation properties of these dyes.[4,5]

Finally, polymethine dyes are a convenient model for the theory of the colour of organic compounds. Systematic investigation of the dependence of the colour of polymethines on their structure has made it possible to test a number of important postulates of this theory: the influence of the electronic symmetry of the chromophores, the intermolecular steric hindrance, and the presence of neutral solvents (solvatochromism) on the colour.[6] Furthermore, it has been shown that certain spectral anomalies of polymethine dyes are caused by the *cis–trans* isomerism.

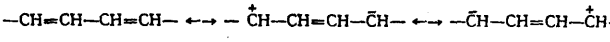
However, despite the fact that the study of the conformational features of polymethine dyes is of both theoretical and practical importance, special reviews on this topic have not so far been published. Isolated non-systematic data may be found in the review of Sturmer and Heseltine.[1] X-Ray diffraction data for a series of cyanines are presented in Smith's review[7] and their photoisomerisation is considered in Kuz'min's review.[4]

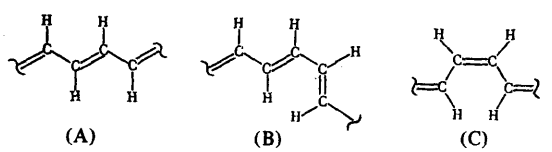
The aim of the present review is comparison of new and old spectroscopic data on the geometrical structure of polymethines and the elucidation of the factors on which it depends. Particular attention has been devoted to a new method for the determination of the conformations of polymethines—from the absorption spectra of dyes with two chromophores.

II. ROTATIONAL ISOMERISM OF COMPOUNDS RELATED TO POLYMETHINES

It is known that the ease of interconversion of atomic groups in the molecule depends on the order of the bond connecting these groups. For example, the barriers to the rotation of various substituted ethane derivatives are in the range 12–75 kJ mol^{-1}, while the barriers to rotation around significantly double bonds are extremely large (120–200 kJ mol^{-1}).[8] Hence, in contrast to the conformers of paraffins, the geometrical isomers of olefins are stable and can be isolated in a pure state. However, olefins tend to undergo photoisomerisation and the ratio of the products in the reaction mixture depends on the extinction coefficient of each isomer at the irradiation wavelength.[9]

The geometrical isomerism of polyenes can involve both double and single bonds. The planar *trans*-configuration (A) or the planar *s-cis*-configuration (B) and the *cis*-configuration (C) of the polyene chain are most energetically favoured; these configurations ensure the maximum interaction of neighbouring π-bonds, which can be represented by the following set of resonance forms:





(A) (B) (C)

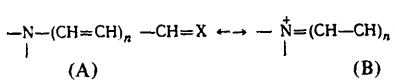
Since the contribution of ionic resonance structures should be small, polyenes are characterised by an appreciable alternation of bond orders. Even a slight shift of electron density is sufficient to increase the barrier to rotation about the central bond from 7.3 kJ mol^{-1} in but-1-ene[10] to 20.5 kJ mol^{-1} in butadiene.[8,10] One should also note that the *trans*-form of butadiene is more stable by 9.6 kJ mol^{-1} than the *s-cis*-form and that at room temperature butadiene exists in the most extended *trans*-form.

As a rule, the absorption bands in the UV spectra of *cis*-polyenes and the cyclised *s-cis*-dienes are less intense than the bands of the fully *trans*-isomers.[9,11] Yet another

characteristic feature of the electronic spectra of *cis*-polyenes is the appreciable short-wavelength absorption—the so called "*cis*-peak".[9] The latter is completely absent from the spectra of *trans*-polyenes owing to the mutual cancellation of the components of the second transition moment, which are equal in magnitude, have opposite directions, and are oriented along the long chain of the molecule.[12] In order to account for the spectroscopic characteristics, it has also been suggested that the model involving the interaction of bound chromophores be used.[13,14] For this purpose, the polyene molecule is divided into two parts relative to the bond involved in the isomerism and each component is regarded as an autonomous chromophore. According to the theory of the interaction of bound chromophores,[13,15] any deviation of the torsional angle from 180° relative to the bond connecting the two chromophores removes the prohibition of the short-wavelength absorption.

Like olefins, polyenes undergo reversible *cis–trans* transitions under the influence of light.[9] Thus the *cis–trans* photoisomerisation constitutes the basis of the transformations of retinal, which play an important role in the visual process.[16]

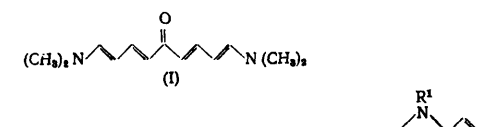
Amides, thioamides, amidines, and their vinylene homologues can serve as examples of compounds with bonds more delocalised than those in polyenes. The electronic structure of these compounds is characterised by an appreciable contribution of the resonance dipolar structure (B):



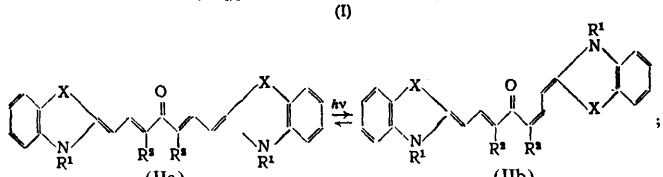
(A) (B)

Depending on the nature of the heteroatom X, the ease of the *s-cis–trans* isomerisation decreases in the sequence NR > O > S, which can be explained by the increased contribution of the structures (B) in the thione. The opposite variation has been found for the rotation about the remaining formally double bonds. For the vast majority of compounds of this kind (for $n > 0$), the isomerisation activation energy is in the range 38–96 kJ mol^{-1} and the acidity of the medium and the steric and the electronic structures of the substituents play a significant role. The relative thermodynamic stabilities of the conformers depend on the nature of the substituents and the dielectric properties of the medium.[8,17]

The ketocyanines (I) and (IIa), whose nature is similar to that of aminopolyvinyl ketones, have the fully *trans*-(*EEEEEEEE*)-structure:[18,19]†



(I)

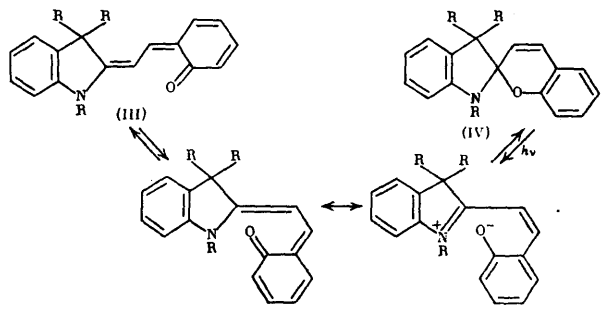


(IIa) (IIb)

X=S, R^1=C_2H_5, R^2=$(CH_2)_3$; X=C$(CH_3)_2$, R^1=CH_3, R^2=H, $(CH_2)_3$, $(CH_2)_3$.

In non-polar solvents the ketocyanines (IIa) undergo photoisomerisation with respect to a bond with a high order, the photoisomer (IIb) being stable and having a deeper but less intense colour compared with the initial form. The activation energy for the reverse reaction depends on the structure of the ketocyanine and also on the strength of the acid used as the catalytic additive and is in the range 41–71 kJ mol^{-1}.[20]

The merocyanines of type (III), formed as a result of the photoinitiated opening of the pyran ring of the spiropyran (IV), are a kind of analogue of aminopolyvinyl ketones:[21]

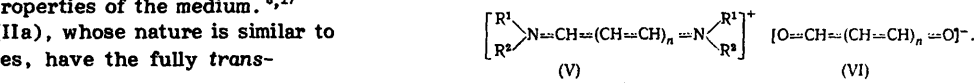


One of the stages in this reversible process is the *cis–trans* isomerisation with respect to the central bond, this stage determining the experimentally observed rate of the dark decolorisation.[22]

III. CONFORMATIONS OF VARIOUS POLYMETHINE DYES

1. Conformations of Streptocyanines

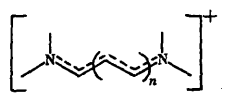
The protonation or alkylation of aminopolyvinylamines leads to the cationic conjugated systems (V)—streptocyanines, which possess "polymethine properties" i.e. their π bonds are fully delocalised and the charges on the atoms of the polymethine chain alternate.[23] The anionic systems (VI), namely oxanines, are also in the "polymethine state". The aminopolyvinyl ketones (thiones) in which the contribution by the dipolar limiting structure is comparable to that of the uncharged structure, i.e. merocyanines, are also close to the "polymethine state":



(V) (VI)

Polymethine compounds are characterised by relatively narrow and intense principal absorption bands, which indicates a comparatively small change in bond lengths on excitation. A second maximum is usually observed on the short-wavelength side of these bands, being separated from the main maximum by 1200–1400 cm^{-1}. It is associated with the vibrational 0–1 transition polarised, like the 0–0 transition, along the axis of the polymethine chain.[24,25]

X-Ray diffraction data have shown that, regardless of the length of the unsubstituted polymethine chain and the presence of substituents at the nitrogen atoms, the cations of the streptocyanines have the fully *trans*-(E_{2n})-conformation with the equalisation of bond lengths characteristic of the "polymethine state" and a slight alternation of the valence angles formed by the sp^2-hybridised carbon atoms:[26–31]



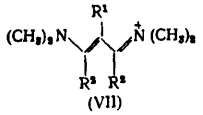
The cations of the streptocyanines investigated are almost planar, which ensures the maximum interaction of the π-electrons and their delocalisation.

† Since different names are used to designate the same conformers of polymethines and related compounds, whenever necessary in the present review the two most frequently employed terms are used for them.

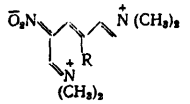
The ^{1}H NMR spectra[32–36] also support the fully *trans*-conformations of compounds (V) and (VI) in solution: the spin–spin coupling constants of the protons of the polymethine chain (12–14 Hz) do not change significantly also after the introduction of the bulky methyl group in the *meso*-position in the polymethine chain of the streptocyanine (V, $n = 2$), which rules out the formation of the *EZEE*-confirmation as a means of eliminating the steric hindrance which has arisen.

A narrow singlet in the ^{1}H NMR spectrum of compound (V, $n = 2$, $R^1 = CH_3$, $R^2 = C_6H_5$), due to aromatic protons, shows that the phenyl groups are arranged at right angles to the plane of the polymethine chain.[33]

The steric structure of the streptocyanines (VIIa, b) has been investigated with the aid of the nuclear Overhauser effect.[37] It has been shown that α,α′-di- and β-monoalkylated trimethine streptocyanines exist in the fully *trans*-(*EE*)-conformation. Compared with the unsubstituted cation, there is some change in the valence angles, which is greater the greater the bulk of the substituent. The distortions of the angles and the deviation of the components of the cation from planarity for equal bulk of the substituent are greater in the α-derivatives (VIIa):



(VII)



(VIII)

$R^1 = H$, $R^2 = H$, CH_3, C_2H_5, iso-C_3H_7 (a); $R^1 = CH_3$, C_2H_5, iso-C_3H_7, t-C_4H_9, $R^2 = H$ (b)

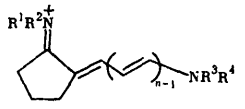
R = H (a); R = NO_2 (b)

Alkyl groups manifest weak electron-donating properties and their influence on the geometrical structure of the polymethines can be explained primarily by steric causes. Substituents such as the nitro-group are capable of being included in the conjugation chain, forming new chromophores and altering therby the conformation of the cation [compounds (VIIIa, b)].[38]

The ^{1}H NMR spectra of the streptocyanines (V, $R^1 = R^2 = CH_3$, $n = 1$, 2) exhibit two signals due to the protons of the methyl group at room temperature and for $n = 3$ also at a reduced temperature. The magnetic non-equivalence of these protons is caused by the hindered rotation of the methyl groups about the C·····$N(CH_3)_2$ bonds. With increase of the length of the polymethine chain, the barrier to rotation diminishes from 70 kJ mol^{-1} ($n = 1$) to 47 kJ mol^{-1} ($n = 3$). An increase in the acidity of the medium reduces the activation energy for the first compound to 36 kJ mol^{-1}. Experimental results[39,40] agree with data obtained by the *ab initio* calculation of the activation energies for the rotation of the amino-groups.[41]

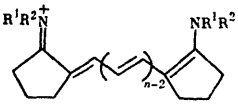
The electronic spectra of streptocyanines (V) cannot serve as a reliable criterion of their conformational homogeneity at room temperature, because instances of the overlap of the bands of isomers absorbing at close wavelengths are possible. A decrease of temperature as a rule causes a narrowing of the absorption bands as a result of the decrease of the amplitudes of low-frequency vibrations.[42] The appearance of inflections on the long-wavelength slopes of the principal bands was noted under these conditions [compounds (V), $n = 2$, 2, $R^1 = R^2 = (CH_2)_{3-5}$].[43] The authors[43] attribute such local maxima to the thermodynamically less stable mono-*cis*-conformers. The absorption bands of streptocyanines with shorter ($n = 0$, 1) chains do not inhibit such splitting. Apart from the principal long-wavelength band, the spectrum of compound (V, $n = 3$) shows yet another specific band in the region of shorter wavelengths, whose intensity increases on heating. By analogy with the short-wavelength absorption of *cis*-polyenes, this band has been called the "*cis*-peak" and has been assigned to absorption by the unstable *cis*-conformers, whose concentration in the equilibrium mixture increases with increase of temperature.

The fixation of the polymethine chain of streptocyanines in the mono-*cis*-($ZE_{2n-2}E$)-configuration (IX) and the di-*cis*-($ZE_{2n-2}Z$)-configuration (X) also leads to a bathochromic shift of the principal absorption band. Although the electronic influence of the substituent (the cyclic trimethylene group) also contributes to the magnitude of this shift, it is believed[44] that the contribution amounts to only half of the overall shift. The oscillator strength of the principal absorption band decreases in the sequence *trans* > *cis* > di-*cis*. The experimental results have been confirmed by LCAO-MO calculations.[44] Unfortunately the authors[44] did not pay attention to the short-wavelength part of the spectrum, where the appearance of "*cis*-peaks" on passing from the *trans*- to the *cis*-form might have been expected:



(IX)

$R^1, R^2 = CH_3, (CH_2)_4$; $R^3, R^4 = CH_3, C_6H_5, (CH_2)_4$

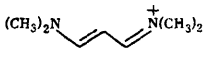


(X)

$R^1, R^2 = CH_3, (CH_2)_4$

Characteristic changes in the absorption spectra of streptocyanines occur when their solutions are irradiated at the wavelength of the absorption maxima.[43,45–49] It has been established that this entails the appearance of a new band, which is displaced to longer wavelengths relative to the first and is characterised by a smaller oscillator strength. In many instances the appearance and increase of the intensity of the new band are accompanied also by the appearance and increase of the intensity of the bands of the "*cis*-peaks" polarised at right angles to the principal band.[43,45] The photochemical reaction is reversible and the rate of the dark reaction increases with increase of temperature and depends on the viscosity of the solvent. The process activation energies are in the range 58–67 kJ mol^{-1}. An increase of the acidity of the medium lowers this energy to 42 kJ mol^{-1}.[48] These spectroscopic data can be readily interpreted within the framework of the *cis–trans* isomerisation of streptocyanines, although the formation of the excimers of these compounds on excitation has been postulated.[49] However, photoisomerisation is supported by the activation energy, which is intermediate between the barriers to rotation about the double and single bonds, which corresponds to a bond order of 1.5 in the "polymethine state".

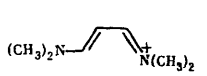
The phototropic mono-*cis*-(*EZ*)-form (XI) of the streptocyanine (V, $n = 1$, $R^1 = R^2 = CH_3$) has been compared with the di-*cis*-(*ZZ*)-form (XII), which is known to be stereohomogeneous.[43,46]



(V)

$\nu_{max} = 31750$ cm^{-1}

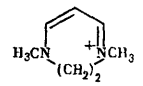
$f = 0.63$



(XI)

$\nu_{max} = 29400$ cm^{-1}

$f = 0.47$



(XII)

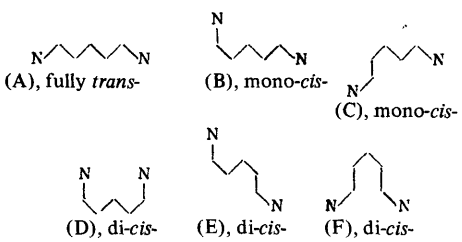
$\nu_{max} = 28400$ cm^{-1}

$f = 0.27$

A distinct bathochromic shift and a decrease of the oscillator strength are observed on passing from the *trans*- to the di-*cis*-form.

The same behaviour is reflected qualitatively by the results of the LCAO-MO calculation for certain conformers of pentamethine streptocyanine.[50] According to the calculated data, the energy of the ground state of the conformer increases in the sequence (A)–(F) and the bathochromic shift of the

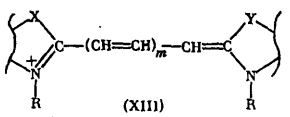
absorption band should take place in approximately the same order:



Calculation has also shown that the rotation around the central bonds of pentamethine streptocyanine requires the expenditure of 61 kJ mol^{-1}, while the rotation about the remaining C⋯⋯C bonds requires 58 kJ mol^{-1},[43] which is in fair agreement with experimental data.

2. Conformations of Monomethine Cyanines

True cyanines of type (XIII) differ from streptocyanines by the fact that the terminal nitrogen atoms, adjoining the polymethine chain, are at the same time components of heterocyclic nuclei.



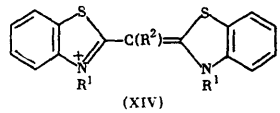
(XIII)

X, Y = O, S, $C(CH_3)_2$, CH=CH, NR; R = H, Alk, Ar

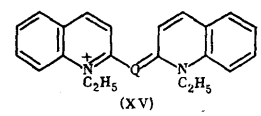
The closest methine group is also incorporated in the heterocyclic ring, so that the cyanine with *m* vinyl group corresponds to the streptocyanine with $n = m + 1$ vinyl groups.

On passing from simple cyanines to compound (XIII), i.e. on replacement of a hydrogen atom by a bulky group X or Y, the steric interaction of the cation intensifies in the first place and the possibility of twisting about the C⋯⋯N bond vanishes in the second place. Furthermore, in asymmetric cyanines ($X \neq Y$) the "polymethine state" differs from the ideal state, namely an alternation of bond orders arises and is more pronounced the greater the difference between the basicities of the terminal heterocycles.[51] The latter factor merits attention because a decrease of the order of a bond facilitates rotation about the latter.

The steric interaction of the heterocyclic nuclei with one another is especially characteristic of monomethine cyanines (XIII, $m = 0$). According to X-ray diffraction data, the steric structure of the cations of monomethine cyanines depends primarily on the effective bulk of the groups X and Y in the terminal heterocycles and also on the presence of a substituent at the carbon atom linking these groups.[52-58] Thus the chromophores of monomethine cyanines (XIV, $R^1 = CH_3$, C_2H_5, $R^2 = H$) have the almost planar fully *trans*-(*EE*)-structure.[52,53] The same conformation obtains in the cation (XV, Q = CH), but, owing to the steric interaction of the hydrogen atoms in the 3 and 3'-positions, the planar structure is distorted (the central torsional angle increases to 50°). The angles between the planes of the heterocyclic rings and the C(2)C(9)C(2') plane are the same.[54] On the other hand, the angles of rotation of the heterocyclic nuclei relative to the C(2)PC(2') plane in the phosphorus-containing analogue (XV, Q = P), which also has the *trans*-(*EE*)-structure, are 40° and 24°, which means that the positive charge is displaced towards the first nucleus; this is also indicated by the proximity of the anion to it.[55]

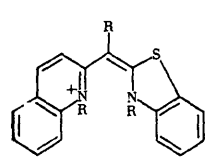


(XIV)

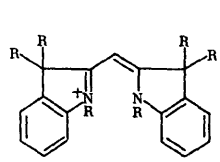


(XV)

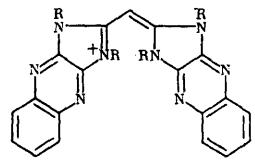
The appearance of a bulky substituent at the *meso*-carbon atom precludes the formation of a planar structure of the cation owing to the strong steric hindrance. Furthermore, the most favourable form in which the cations of the *meso*-methylthiaquinocyanine (XVI) exist in the crystal is the di-cisoid form, in which the angle between the planes of the heterocycles is 60°.[56]



(XVI), R = CH_3



(XVII), R = CH_3

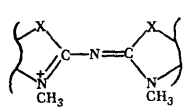


(XVIII), R = C_2H_5

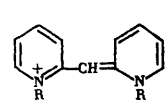
The strong steric interactions of the isopropylidene groups in the hypothetical *trans*-form of monomethine indocyanine are the cause of the non-planar di-*cis*-(*ZZ*)-structure of the cation (XVII). The dihedral angle between the planes of the indolenine rings is 48°.[57]

The monomethine cyanines (XVIII) with terminal 1,1',3,3'-tetraethylimidazo[4,5-*b*]-quinoxalinium nuclei, which are at an angle of 55°, also belong to non-planar dyes. In view of the high symmetry of the cation, all its conformations are degenerate.[58]

The number of signals of the *N*-alkyl groups can serve as a criterion for the selection of a particular conformation on the basis of ^1H NMR spectra. Thus a single signal due to *N*-methyl groups has been detected in the ^1H NMR spectra of monomethine quino-, oxa-, and thia-cyanines, which demonstrates, according to the author,[59] the *trans*-(*EE*)-configuration of these compounds. The introduction of a bulky alkyl substituent at the *meso*-carbon atom entails the splitting of this peak, which indicates the mono-*cis*-(*ZE*)-structure of the *meso*-substituted monomethine cyanines in solution. A similar splitting has been observed[59] for the aza-cyanines (XIX) and also for monomethine pyridocyanine (XX, R = CH_3). The simple structure of the ^1H NMR spectra in the regions corresponding to the resonance of the protons of the ethyl group and also comparison of the observed and calculated "aromatic" components of the spectrum permit the conclusion that compound (XX, R = C_2H_5) and its meso-analogue exist exclusively in the *trans*-(*EE*)-form:[60]



(XIX)



(XX)

The influence of the steric structure of substituents on the principal characteristics of the absorption spectra of monomethine cyanines has been observed in a number of studies.[2,61,62] It was found that the sterically unhindered monomethine thiacyanines (XIV, $R^1 = H$, $R^2 = H$ or CH_3; $R^1 = CH_3$, $R^2 = H$) have approximately the same absorption maximum at 425 nm, while the steric interactions in the sterically hindered dyes (XIV, $R^1 = R^2 = CH_3$) lead to an appreciable bathochromic shift of the band. The same pattern has been observed for

a series of quinoline dyes. The possibility of the existence of various conformations of the sterically hindered dications has been postulated, but the spectroscopic shifts have been accounted for exclusively by a greater or lesser deviation of the components of the cation from the planar disposition.[2,61]

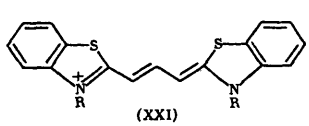
In contrast to this, Scheibe et al.[62] attribute all the spectroscopic changes for a series of monomethine pyrido- and quinocyanines exclusively to transitions to particular conformations. The choice of the geometrical structure of the cations in the above study[62] was based on the oscillator strength. The authors[62] justly assume that, by analogy with streptocyanines, the absorption intensity decreases in the series of structures *trans* > *cis* > di-*cis*. However, they compared dyes which differ both in their electronic structure and in the influence of substituents, on the one hand, and in their tendency towards solvation, on the other. Nor has any account been taken of the fact that the decrease of the absorption intensity can result not only from a *trans–cis* transition but also on distortion of the planar structure of the polymethine chain.

The study of the absorption bands of monomethine cyanines has shown that, in assigning the postulated conformers, one should take into account the short-wavelength part of the spectrum, since the presence of the "*cis*-peaks" can serve as proof of the presence of *cis*-forms. However, this procedure requires careful selection of the objects of comparison.[45,63] It has been noted[45,64] that monomethine cyanines do not undergo a photoisomerisation resembling that of streptocyanines or such photoisomerisation takes place with an extremely low quantum yield.

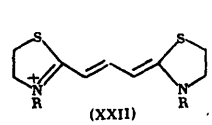
3. The Conformations of Carbocyanines and Their Vinylene Analogues

The carbocyanines (XIII, $m = 1$) are pentamethine streptocyanines as regards the length of the polymethine chain and differ from the monomethine cyanines in that the conformational transitions in their cations can take place via both the central and peripheral bonds of the polymethine chain.

X-Ray diffraction analysis of the thiacarbocyanines (XXI) unsubstituted in the polymethine chain has shown that their cations have exclusively the fully *trans*-(*EEEE*)-structure and are almost planar. According to different data, the dihedral angles between the planes of the heterocyclic nuclei and the plane of the remaining atoms of the chromophore range from 3° to 12°.[65–69] These angles depend on the effective bulk of the *N*-alkyl groups. Thus the replacement of an ethyl group by a methyl group leads to an appreciable flattening of the cation.[67,68] The *EEEE*-conformation of the chromophore is also realised in the crystal of thiazolinocarbocyanine (XXII). The polymethine chain and one of the heterocyclic nuclei then have a planar structure, while the second nucleus has the half-chair form.[70]



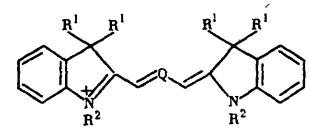
(XXI)
R = CH_3, C_2H_5



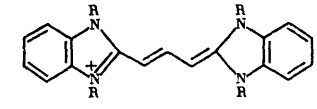
(XXII)
R = C_2H_5

The indocarbocyanine (XXIIIa, Q = CH) also has a transoid structure in the crystal. The dihedral angle between the planes of the indoline nuclei is 13.8°. In the aza-analogue (XXIIIa, Q = N), this angle is 13.3°, while in compound (XXIIIa, Q = P) it amounts to 15.1°. In another crystalline modification, formed by the dyes (XXIIIa, Q = P or As), this angle diminishes to 6.8° and 6.3° respectively.[71]

The deviation of the planes of the heterocyclic nuclei in the crystal of imidocarbocyanine (XXIV) by 8° from one another is caused by the weak steric interaction of the ethyl groups.[72]



(XXIII)
$R^1, R^2 = CH_3$ (a); $R^1 = CH_3$, $R^2 = C_2H_5$ (b)



(XXIV)
$R = C_2H_5$

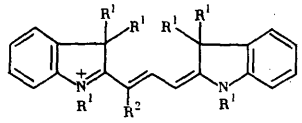
^{1}H NMR data for unsubstituted carbocyanines rule out the mono-*cis*-conformation with respect to the central bond, because the spin–spin coupling constant for the protons of the polymethine chain is 12–14 Hz and the mono-*cis*-conformation with respect to the peripheral bonds is ruled out owing to the equivalence of the *N*-alkyl groups.[73–75] The study of the indocarbocyanines (XXIIIb, Q = CH, N, or P) with the aid of the nuclear Overhauser effect has made it possible to rule out also the symmetrical di-*cis*-(*EZZE*)-form of these compounds.[76]

The conformational homogeneity of the unsubstituted thiacarbocyanines has been confirmed also by the fact that their absorption,[77–79] emission, and fluorescence excitation[79] spectra, recorded at room temperature, are virtually identical with the spectra obtained at a low temperature.

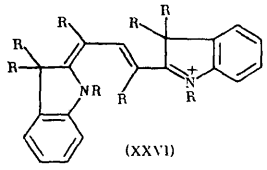
The pulsed photoexcitation of the cations of sterically unhindered carbocyanines leads to the appearance of short-lived *cis*-isomers, whose absorption bands have undergone a bathochromic (oxacarbocyanines) or hypsochromic (thiacarbocyanines) shift relative to the parent bands.[4,48,77,80–83] The activation energy for the reverse dark reaction is 50 kJ mol^{-1} for oxacarbocyanine and 63 kJ mol^{-1} for thiacarbocyanine.[84] The introduction of electron-donating substituents in the 6,6′-positions in the benzothiazole rings increases the activation energy, while the introduction of electron-accepting substituents diminishes it. This finding has been explained by the corresponding increase or decrease of the bond orders in the polymethine chain; here it is assumed that the photoisomerisation of carbocyanines unsubstituted in the polymethine chain involves the peripheral 2- and 8-positions.[82] In the photoisomerisation of asymmetric dyes, the activation energy for the *cis* → *trans* relaxation decreases with increase of the difference between the basicities of the terminal heterocycles. Since this is accompanied simultaneously by an enhancement of the alternation of bond orders in the polymethine chain, it is assumed[83] that the dark isomerisation involves a bond with a reduced order, i.e. takes place outside the more basic nucleus.

The introduction of a substituent in the α-position in the polymethine chain of the carbocyanine leads to a steric interaction of the substituent with fragments of the heterocyclic nucleus and the polymethine chain. In the crystals of α-ethylindocarbocyanine (XXV), the energy of such interaction is insufficient for the isomerisation of the cation and the latter therefore exists in a distorted fully *trans*-(*EEEE*)-conformation. The presence of a second substituent in the α′-position precludes the existence of the fully *trans*-form, probably owing to the steric interaction of the substituents, while the crystal of the cation (XXVI) exists in the di-*cis*-(*ZZEE*)-form, the dihedral angle between the planes of the

heterocyclic nuclei amounting to 34.7°.[84]

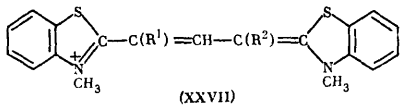


(XXV)
$R^1 = CH_3$, $R^2 = C_2H_5$



(XXVI)
$R = CH_3$

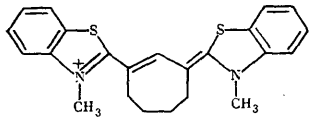
An attempt has been made to separate the steric and electronic effects of the substituents in the α- and αα′-positions in the polymethine chain on the basis of the absorption spectra of the thiacarbocyanines (XXVII).[85-88]



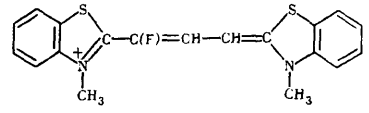
(XXVII)

R^1=H, CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_6H_5, OCH_3, Cl, $NHCOC_6H_5$, $N(CH_3)C_6H_5$, $COOC_2H_5$ CHO, C_6H_4N, SC_2H_5, SC_6H_5; R^2=H, CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_6H_5, OCH_3, SC_6H_5, Cl, $NHCOC_6H_5$, $N(CH_3)C_6H_5$.

The introduction of a substituent of any electronic type as a rule induces a hypsochromic shift of the absorption maximum of the thiacarbocyanine (XXVII). The influence of a similar second substituent in the α′-position is not the same as that of the first and not only quantitatively but also qualitatively. It has been suggested[85,86] that the influence of a single substituent is associated with the breakdown of the electronic symmetry of the chromophore, while the spectroscopic changes in disubstituted dyes are determined by the competition between the electronic nature of the substituents and the steric hindrance to the planar disposition of the cation. Such hindrance commences on monosubstitution and intensifies on disubstitution, which is indicated by the corresponding decrease of the absorption intensity. The *cis–trans* isomerisation, which is most likely to involve peripheral bonds of the polymethine chain, probably contributes to the spectroscopic shifts. This is indicated[87] by the almost identical absorption of solutions of αα′-diethylcarbocyanine (XXVII) and the dye (XXVIII) with a seven-membered ring in the chromophore.



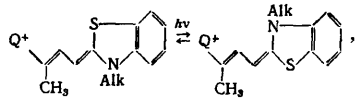
(XXVIII)



(XXIX)

A mixture of the *cis*- and *trans*-isomers of α-fluorothiacarbocyanine (XXIX) was detected from the absorption spectra at a low temperature.[88]

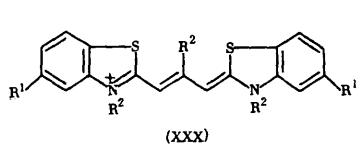
The photoisomerisation of α-substituted carbocyanines proceeds with a high quantum yield, close to that for the unsubstituted compounds. It has been suggested that the photoisomers of the compounds compared have the same nature, i.e. are *EEZ*-isomers and that the isomerisation involves the unsubstituted 2- and 8-positions:[4,89,90]



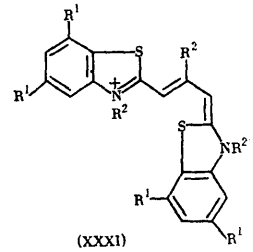
where Q is a heterocyclic nucleus.

The introduction of a bulky substituent in the β-position in the polymethine chain also intensifies the steric interaction of the fragments of the carbocyanine cation. There has been a considerable growth of interest in dyes of this kind, because β-ethylthiacarbocyanine proved to be an effective sensitiser of silver halides.[1-3]

According to X-ray diffraction data, the thiacarbocyanine cation (XXX) has a distorted *EEEE*-structure. Compared with the unsubstituted dye (XXXI), the distance between the sulphur atoms is increased owing to the repulsion of the latter from the ethyl group separating them.[91] In contrast to this, the thiacarbocyanine (XXXI) exists in the solid phase in the non-planar mono-*cis*-(*EEZE*)-form.[3,92]



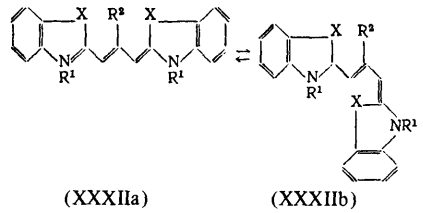
(XXX)
$R^1 = Cl$, $R^2 = C_2H_5$



(XXXI)
$R^1 = CH_3$, $R^2 = C_2H_5$

The β-phenylthiacarbocyanine cations exhibit in the crystals the fully *trans*-(*EEEE*) conformation.[93] The phenyl group is then rotated almost at right angles to the long axis of the cation and does not have an appreciable effect on the colour of the dye.[61]

The absorption bands of solutions of β-substituted carbocyanines (XXXII) are split at low temperatures into two bands in close proximity.[78,94-97] The intensity of each band increases on excitation of the neighbouring band by irradiation at the wavelength of its absorption maximum. The cessation of irradiation entails the return of the system to the initial equilibrium state. The experimental data have been interpreted within the framework of the *cis–trans* isomerism of the test compound: steric interaction of the β-substituent with the terminal nuclei increases the energy of the ground state of the *EEEE*-form (XXXIIa) and makes it comparable to the energy of the *EEZE*-conformation (XXXIIb):



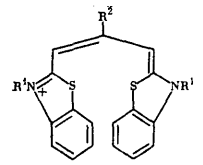
(XXXIIa) (XXXIIb)

X=O, S, Se; R^1=CH_3, C_2H_5; R^2=CH_3, C_2H_5, C_6H_5, OCH_3, SCH_3

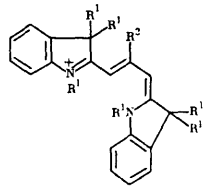
The long- and short-wavelength bands are due to the first and second isomeric forms respectively. The equilibrium position depends greatly on the solvent: the longest *trans*-isomers predominate in weakly polar media, while in strongly polar media they are present only as an admixture to the *cis*-isomer. The luminescence spectra of the carbocyanines (XXXII, R^2 = Alk, OCH_3, or SCH_3) have been investigated over a wide temperature range.[79,95-97] It has been found that the *EEZE*-isomers fluoresce only at a low temperature and that the fluorescence intensity is appreciably lower than for the *EEEE*-isomers.

Analysis of the form and number of signals in the ^1H NMR spectra of β-substituted carbocyanines and also the observation in certain cases of the nuclear Overhauser effect make it possible to determine unambiguously the geometrical structure of the conformers and to estimate quantitatively the position of the conformational equilibrium.[75,98] It has been established that an increase of the effective bulk of the substituent in the β-position promotes an increase of the content of the

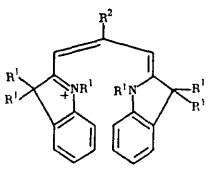
cis-isomer. Thus the concentration of the *EEZE*-isomer of the thiacarbocyanine (XXXII) increases in the sequence $H \ll C_6H_5 < CH_3 < C_2H_5$ as R^2 is altered. As a result of the introduction of the t-butyl group, the thiacarbocyanine cation exists both in solution and in the solid phase exclusively in the form of the non-planar di-*cis*-(*EZZE*)-conformer (XXXIII).



(XXXIII)
$R^1 = C_2H_5$, R^2 = t-C_4H_9



(XXXIV)
$R^1 = CH_3$, $R^2 = CH_3, C_2H_5, C_6H_5$



(XXXV)
$R^1 = CH_3$, R^2 = t-C_4H_9

The concentration of the mono-*cis*-(*EEZE*)-isomer increases with increase of the bulk of the heteroatom X in the carbocyanines (XXXII). Finally, only the tri-*cis*-(*ZEZZ*)-form obtains in β-substituted indocarbocyanines (XXXIV), while in solution it exists in a dynamic equilibrium with the identical *ZZEZ*-form. The cation (XXXIV, $R^2 = CH_3$) has the same conformation in the crystal, the angle between the indolenine nuclei reaching 78°. The symmetrical fully *cis*-(*ZZZZ*)-conformation is fixed in the cations of the carbocyanines (XXXV). According to X-ray diffraction data, the system does not have a planar structure: the average torsional angle between the fragments of the polymethine chain is 19° and the angle between the indolenine nuclei is 41°.[98] The activation energy for the isomerisation processes is in the range 35–62 kJ mol^{-1}.[75,98]

The absorption bands of carbocyanines undergo appreciable changes on β-substitution,[2,61,98] but, among the multiplicity of steric and electronic factors, it is difficult to identify the intrinsic contribution of a particular conformation to the absorption.

The photoisomerisation of β-substituted carbocyanines has been investigated fairly widely.[4,64,80,96,99] The rate of this process for the thiacarbocyanine (XXXII, $R^1 = C_2H_5$, $R^2 = CH_3$) at −125 °C depends greatly on the nature of the halide in the solvent and increases in the sequence $C_2H_5Cl < C_2H_5Br < C_2H_5I$. This factor has been attributed[96] to the triplet mechanism of the isomerisation, whose probability increases in parallel with the increase of the spin–orbital coupling constant induced by the presence of neighbouring atoms with a higher atomic number. This factor has also been used[96] to account for the rapid isomerisation of β-methylselenacarbocyanine compared with β-methylthia- and even more so β-methyloxacarbocyanines.

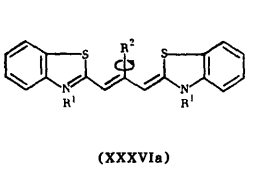
On the other hand, experiments on the triplet–triplet energy transfer have led to the hypothesis[64,99] that a singlet excited state is involved exclusively in the photoisomerisation at room temperature and that its degradation takes place in accordance with the scheme

$$
{}^0S_{trans(cis)} \xrightarrow{h\nu} {}^*S_{trans(cis)} \begin{cases} \rightarrow {}^0S_{trans(cis)} \text{ (fluorescence)}, \\ \rightarrow {}^1T_{trans(cis)} \text{ (intersystem crossing)}, \\ \rightarrow {}^0S_{trans(cis)} \text{ (internal transition)}, \\ \rightarrow {}^0S_{cis(trans)} \text{ (isomerisation)}; \end{cases}
$$

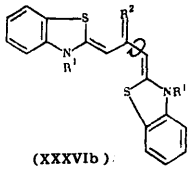
$$
{}^0S_{cis(trans)} \rightarrow {}^0S_{trans(cis)} \text{ (dark reaction)}.
$$

According to this scheme, three radiationless processes compete: isomerisation, internal transition, and intersystem crossing. In carbocyanines, with the exception of β-iodothiacarbocyanine, the last process takes place with an extremely low quantum yield. The main factor determining which of the two first processes predominate is steric hindrance to the planar structure of the photoisomer. In contrast to unsubstituted and α-substituted carbocyanines, in the molecules of β-substituted dyes the dominant process leading to the degradation of the excited state is internal transition. The unusually high quantum yield in the photoisomerisation of β-fluorothiacarbocyanine can be explained by the small size of the fluorine atom, which permits isomerisation with respect to the C(2)–C(8) bond.

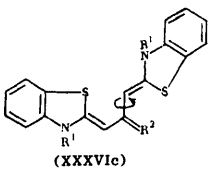
An unusual kind of isomerism, called "allopolar", has been described.[2,100] An obligatory condition for systems having the general formula (XXXVI) and undergoing this type of isomerism is the presence in the polymethine chain of bulky substituents R^2, containing π electrons which can interact under certain conditions with the main π-electron system of the molecule.



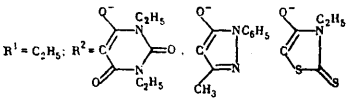
(XXXVIa)



(XXXVIb)

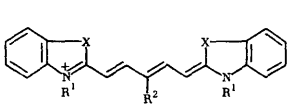


(XXXVIc)

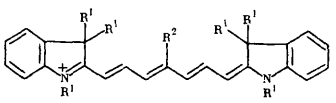


In the betaine (holopolar) form (XXXVIa), the steric interaction between the substituent R^2 and the heterocyclic nuclei makes the plane of the substituent perpendicular to the long axis of the carbocyanine part of the molecule and the influence of the substituent on the electronic absorption spectrum is purely inductive in character. The second isomeric merocyanine form (XXXVIa) is characterised by the fact that the π electrons of the substituent R^2 form a single chromophoric system with one half of the molecule, the second half being perpendicular to the new chromophore. An alternative form is the *trans*-(*EE*)-isomer (XXXVIc). The forms presented above absorb in different parts of the spectrum and this type of isomerism can therefore be observed at room temperature. The ratio of the isomers is sensitive to changes in the dielectric properties of the medium. It has been shown that polar and proton-donating solvents increase the content of the charged form (XXXVIa), while non-polar and aprotic solvents tend to increase the content of the merocyanine forms (XXXVIb, c).

There is little information about the steric structure of the dicarbocyanines (XIII, $m = 2$) and higher vinylene homologues. It is known that the cations of the thiadicarbocyanine (XXXVII, $R^1 = C_2H_5$, $R^2 = H$), indodicarbocyanine (XXXVII, $R^1 = CH_3$, R^2 = cyclopropyl), and indotricarbocyanine [XXXVIII, $R^2 = CH_2CH(OCH_3)_2$] exist in the solid phase in the fully *trans*-conformation and are almost planar.[100–102]



(XXXVII)
X = S, $C(CH_3)_2$; $R^1 = CH_3, C_2H_5$; R^2 = H, OCH_3, C_3H_5, C_4H_7, C_6H_{11}, CH_3, C_6H_5, F, Cl, Br, I, $C_6H_5N_2$, CHO, CN, NO_2



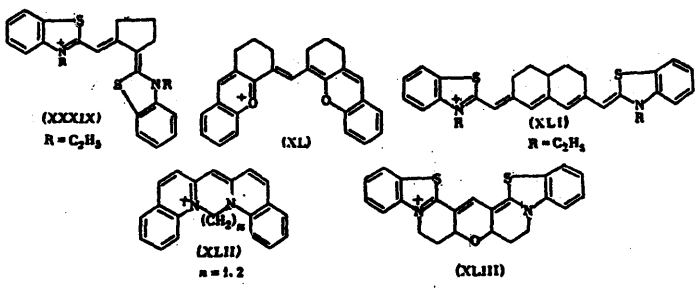
(XXXVIII)
$R^1 = CH_3$; R^2 = H, $CH_2CH(OCH_3)_2$

^1H and ^{13}C NMR studies of various γ-substituted dicarbocyanines (XXXVII) and also the indotricarbocyanine (XXXVIII, $R^2 = H$) have shown that these compounds exist in solution exclusively in the fully *trans*-conformation, favouring, other conditions being equal, the maximum overlap of the orbitals

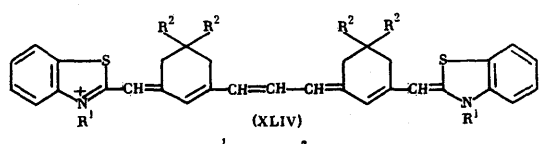
and the delocalisation of π electrons.[103-106] These data conflict with the earlier report[109] of the separation of three isomers by chromatographing thiatricarbocyanine on calcium carbonate at room temperature.

Only the photoexcited forms of the stereoisomers of the dicarbocyanines, which as a rule absorb at longer wavelengths than the corresponding forms in the ground state, can be detected.[4,80,110,111] The number of possible steric forms of dicarbocyanines is much greater than for dyes with a shorter polymethine chain. Thus the indodicarbocyanines (XXXVII, R^2 = H or F) give rise to several forms—short-lived (lifetime $\tau = 10^{-6}$ s) and long-lived ($\tau = 10^{-2}$ s).[111] The unstable photoisomers have the sterically highly hindered and therefore non-planar di-*cis*-structure. The angle of rotation of the chromophore fragment is closer to 180° on formation of the long-lived photoisomers but the latter are not fully planar either.

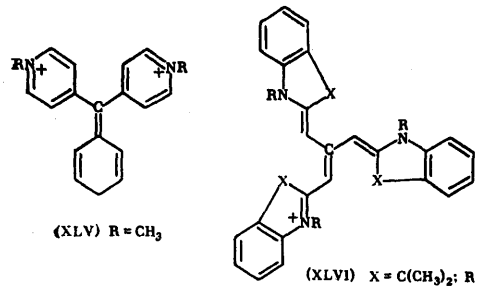
This factor is precisely the reason why the photoisomers fluoresce much less effectively than the corresponding forms in the ground state. This leads to losses in the excitation band owing to the overlap of the fluorescence spectrum of the generating form in the ground state and the absorption spectrum of the photoisomer. Another cause of the impairment of the generating properties of polymethine dyes is the "depletion" of the first excited singlet state owing to losses in the isomerisation proper.[4,5,112,113] These causes may be eliminated by the partial [the cations (XXXIX)–(XLI)] or complete [the cations (XLII) and (XLIII)] fixation of the chromophore in a particular conformation.[114-119]

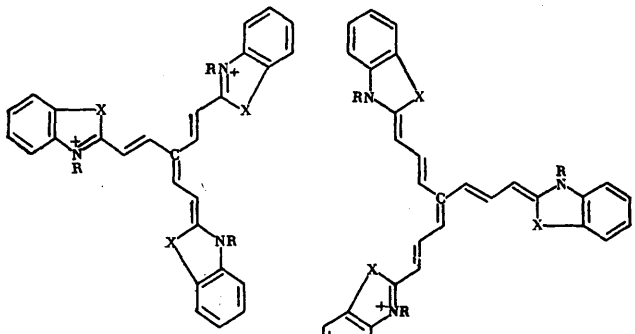


Taking into account the entropy factor, it might have been supposed that an increase in the length of the polymethine chain would reduce the probability of the existence of the di-cations in the fully *trans*-conformation, as happens, for example, in the molecules of saturated linear hydrocarbons.[8] Thus the short-wavelength absorption of the cation (XLIV) has been explained[120] by the existence of the *cis*-isomer. On the other hand, recent studies[121,122] have shown that polycarbocyanines exist in solution in the form of solvates absorbing in different parts of the spectrum.



The so-called trinuclear dyes (XLV)–(XLVIII) constitute a special group. They differ by the fact that the *meso*-substituent is yet another heterocyclic nucleus linked directly to the polymethine chain [compound (XLV)] or via the methine [compound (XLVI)], vinylene [compound (XLVII)], or propenylene [compound (XLVIII)] groups. It has been shown from NMR data that the cations or di-cations of these compounds have a propeller-like structure and possess a three-fold symmetry axis passing through the central carbon atom.[60,102,103,123] This configuration of the cation (XLVIII) is realised in the crystal.[102]

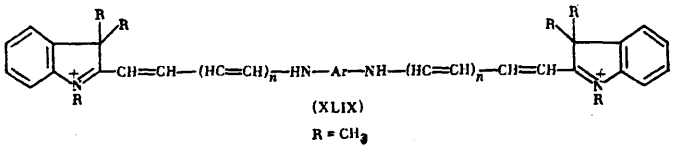




IV. ABSORPTION SPECTROSCOPIC STUDY OF THE CONFORMATIONAL FEATURES OF POLYMETHINE DYES WITH TWO CHROMOPHORES

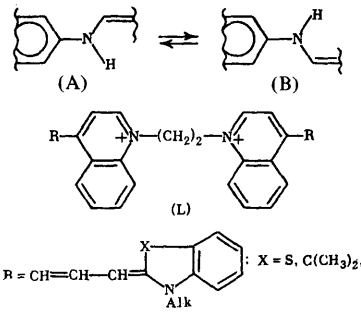
As mentioned above, electronic spectra proved to be relatively unsuitable for the investigation of the conformations of polymethine dyes owing to the multiplicity of factors masking the contribution of the particular conformation to the absorption. On the other hand, the phenomenon of the interaction of chromophores, discovered by Kiprianov and Mushkalo,[124] showed that the scope of electronic spectroscopy can be greatly increased. A fundamentally new approach to the problem of the study of the conformations of polymethines is based on the characteristic features of the interaction of chromophores bound in a single molecule, in particular on the postulate that the ratio of the intensities of two absorption bands is determined ay the angle between the directions of the chromophores (ADC) in the cation.[15]

The spectroscopic properties of the readily available hemicyanines (XLIX, n = 0 or 1), which can be regarded as streptocyanines with rigidly fixed terminal arene nuclei, were investigated in the first place:



After varying the relative positions of the chromophores in structural isomers by introducing an aryl or heteroaryl connecting nucleus, by introducing various substituents into

the latter, and by altering the solvation properties of solvents, the authors[124-132] concluded, from the ratio of the intensity of the two absorption bands, that the conformational equilibrium between the two planar forms (A) and (B) of the hemicyanine fragment is very mobile and depends on all the factors enumerated.



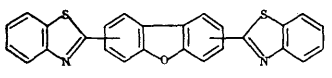
(A) (B)

(L)

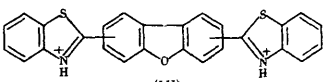
The conformations of the biscarbocyanine (L), in which the heterocyclic nuclei are linked by a polymethine bridge, have been discussed.[132] As in the spectra of bishemicyanines, the ratio of the intensities of the longest-wavelength absorption band in the spectrum of this dye depends on the ADC in each conformer, formed as a result of the hindered rotation about the single bonds in the ethylene connector, and also on the concentration of a particular conformer. It has been shown that an increase of solvent polarity is accompanied by an increase of the intensity of the short- at the expense of the long-wavelength band, i.e. by a shift of the conformational equilibrium towards the formation of skewed (*gauche*) conformers.

The shift towards the formation of the more "compact" conformer (L) takes place also when a high pressure is applied to the solution of the dye.[133]

The absorption spectra of the highly coloured dibenzothiazolyldibenzofurans (LI) and their simple salts (LII) have been examined within the framework of the theory of the interaction of chromophores. The positions and intensities of the bands in the spectra of all the possible planar conformers, formed on rotation of the benzothiazole groups about the bonds with the dibenzofuran nucleus, have been evaluated by quantum-chemical calculation.[134]



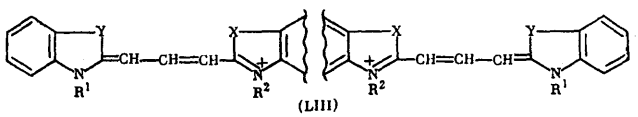
(LI)



(LII)

Unfortunately the broad overlapping absorption bands hinder the interpretation of the spectra of the majority of the compounds mentioned.

The biscarbocyanines (LIII), in which the central nucleus has a rigid structure and which give rise to narrow well resolved absorption bands, proved to be a much more successful model for the study of the characteristic features of the interaction of chromophores:[6,15,135,136]

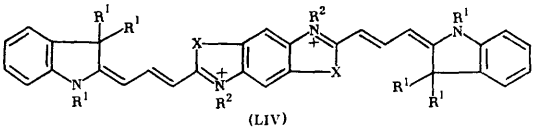


(LIII)

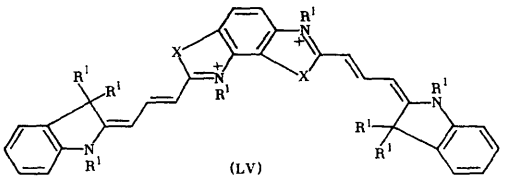
X, Y = O, S, $C(CH_3)_2$; R^1, R^2 = CH_3, C_2H_5

These systems proved to be extremely suitable also for the solution of conformational problems.[137-140]

The fact that the fully *trans*-conformation is the only one for both polymethine chains of the biscyanines (LIII) has been confirmed by the complete similarity of the forms of the absorption curves within each of two families of dyes (LIV) and (LV) in which the ADC should be identical for structural reasons regardless of the bond lengths and valence angles.[137]



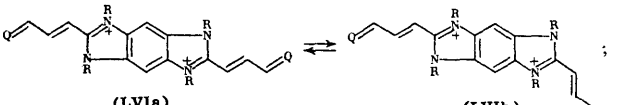
(LIV)



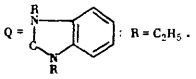
(LV)

X = O, S, $C(CH_3)_2$; R^1 = CH_3; R^2 = CH_3, C_2H_5

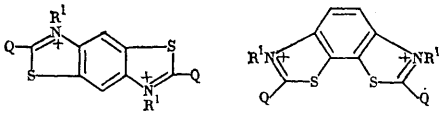
The identity of the forms of the absorption curves is consistent with the presence of one and only one conformation of the chromophores. The presence in solution of several conformers, each of which has its own ADC, should ultimately affect the ratio of the band intensities. For example, by virtue of its high symmetry, the biscyanine (LVI) can exist in two almost equally probable forms (LVIa) and (LVIb), in one of which the ADC is 180° and in the other 120°. An appreciable short-wavelength band is observed precisely because of the conformational inhomogeneity in the absorption spectrum of the biscyanine (LVI).[137]



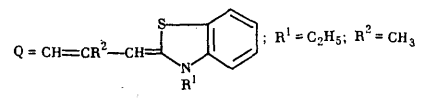
(LVIa) (LVIb)



The synthesis and spectroscopic study of the biscarbocyanines (LVII) and (LVIII) with bulky substituents in the β-position in the polymethine chain made it possible to observe the conformational equilibrium between the fully *trans*- and *cis*-forms at room temperature without resorting to special measuring techniques.[137] In the former case the conformational homogeneity is manifested by a distinct short-wavelength band. The presence of this band rules out the possibility that steric hindrance may be eliminated exclusively as a result of the alteration of the valence angles between the atoms of the polymethine chain, since in this case the ADC of 180° would have been retained.



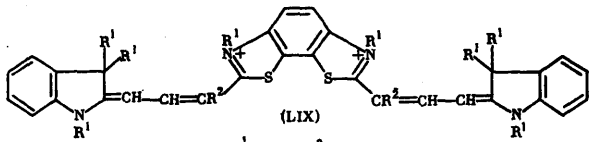
(LVII) (LVIII)



R^1 = C_2H_5; R^2 = CH_3

The introduction of a methyl group in the α-position in one and then in the other polymethine chain [in the dyes (LIX)] make it possible to follow the appearance of the corresponding

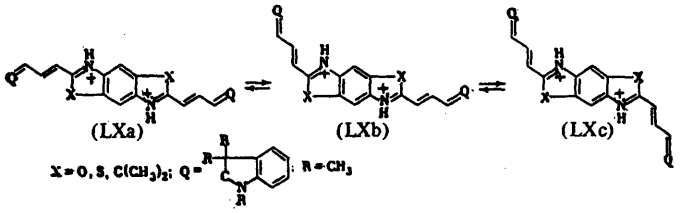
cis-isomers from the relative increase of the intensity of the long-wavelength band.[137]



(LIX)

$R^1 = CH_3$; $R^2 = H, CH_3$

The appearance of *cis*-conformations in the two previous cases (α- and β-substitution) is associated with the increase in the steric interaction in the di-cations. The example of NH-biscyanines shows, on the contrary, that conformational inhomogeneity can arise on replacement of the bulky methyl group at the nitrogen atoms of the terminal heterocycles by a hydrogen atom.[138–140] Thus there is no short-wavelength band in the spectrum of *N*-methylated dyes (LIV). This is consistent with the fully *trans*-disposition of both polymethine chains, forming an angle of 180°. However, for the NH-biscyanines (LX) this *trans,trans*-conformer (LXa) is only one of the three possible conformers. Although another conformer (LXc), corresponding to the *cis*-configuration of each polymethine chain, also does not contribute to the short-wavelength absorption, the chromophores of the non-centrosymmetric *cis,trans*-conformer (LXb) form an ADC less than 180°; the short-wavelength band of this particular conformer is in fact partly allowed. If instead of conformational changes the fully *trans*-polymethine chains were fully displaced into the space previously occupied by methyl groups, the ADC would have remained 180° and the prohibition of the short-wavelength band would have remained in force:

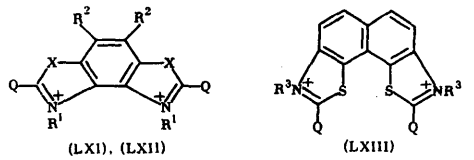


(LXa) (LXb) (LXc)

X = O, S, $C(CH_3)_2$; Q = ; R = CH_3

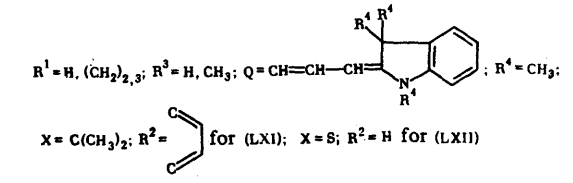
The conformational changes can be followed most clearly from the absorption spectra of biscyanines with angular central nuclei.

The considerable predominance of the long- over the short-wavelength band in the absorption spectra of the biscyanines [LXI, $R^1 = (CH_2)_{2,3}$] is determined by the obtuse ADC, to which correspond the *trans*-conformations of both polymethine chains. The replacement of the alkylene bridge by hydrogen atoms [in the dye (LXI, $R^1 = H$)] leads to the inversion of the intensities of the bands with retention of their positions. This is caused by the presence in the equilibrium mixture of the conformer (LXI) whose polymethine chains are in the *cis*-conformations and form an acute angle.



(LXI), (LXII)

(LXIII)



$R^1 = H, (CH_2)_{2,3}$; $R^3 = H, CH_3$; $Q = CH{=}CH{-}CH$; $R^4 = CH_3$;

X = $C(CH_3)_2$; R^2 = for (LXI); X = S; $R^2 = H$ for (LXII)

The bisthiacyanines (LXII) are structural analogues of the dyes (LXI) but the redistribution of band intensities on passing to NH-biscyanine is not so great. This is associated with the smaller fraction of the *cis,cis*-conformer in the thiazole dye compared with the pyrrolenine dye.[140]

On the other hand, appreciable spectroscopic changes occur after the gradual replacement of the *N*-methyl groups by hydrogen atoms in bisthiacarbocyanines (LXIII). Calculation of the conformational equilibrium[140] has shown that the fraction of the *cis*-conformers of the dyes (LXIII) is greater than for the remaining NH-cyanines derived from benzobisthiazoles. This is caused by the mutual repulsion of chromophores bearing like charges, which is a maximum for conformers with chromophores in structural proximity and a minimum for conformers such as (LXa) and (LXc), i.e. with chromophores remote from one another. In the latter case the conformational equilibrium depends on the steric factor, which is determined by the relative dimensions of the groups NH and X. The Coulombic repulsion of the chromophores is also the cause of the distinct dependence of the conformational equilibrium on the dielectric properties of the medium.[138–140]

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Thus it is now possible to identify the main factors on which the steric structures of polymethine dyes depend, including their tendency to exist in the form of different conformers. These are the nature of the terminal heterocyclic nucleus and the substituent at its nitogen atom, the length of the polymethine chain, the effective bulk of the substituent and the site where it is introduced, the properties of the medium, and also the molecular interaction (the possibility of aggregation).

However, despite the evident advances which have been achieved as the spectroscopic technique has been improved and new systems have been synthesised, the identification of conformers remains a fairly complex task to this day. In view of the low activation barrier of the isomerisation process (33–63 kJ mol^{-1}), it is not possible to separate the conformers and to isolate them in a pure state. X-Ray diffraction analysis requires special conditions as regards the preparation of crystalline specimens, which frequently cannot be fulfilled. The geometrical structure of the di-cations in the crystal can differ appreciably from their state in solution. The electronic spectra, which are the most important characteristics of the dyes, are relatively unsuitable in this instance. The amount of information derivable from them increases appreciably in the case of biscyanines, but this involves considerable difficulties in the synthesis of suitable objects. A more effective method for the determination of the steric structures of methine dyes is NMR.

In the future one may probably expect that studies devoted to the conformational analysis of cyanines with non-traditional heterocyclic nuclei and also containing a wider range of substituents will be carried out. The problems postulated will be solved by improving and employing on a wider scale the physicochemical and special synthetic methods.

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Institute of Organic Chemistry,
Academy of Sciences of the
Ukrainian SSR,
Kiev