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Some Approaches to the Construction of New Nitrogen-containing Heterocyclic End Groups for Synthesizing Polymethine Dyes Absorbing in the IR Region

Yu. L. Briks, E. K. Mikitenko & N. N. Romanov*

Institute of Organic Chemistry, Academy of Sciences of the Ukraine, 253660, Kiev-94
Murmanskaya 5, Ukraine

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ABSTRACT

The development of methods of synthesizing new heterocyclic derivatives suitable for obtaining polymethine dyes is described. Compounds of this series are shown to have potential for the synthesis of deeply colored dyes, and which although having a short polymethine chain, absorb in the IR region. It is shown that structural modifications within the dyes enables the position of their absorption bands to be controlled over wide regions. © 1997 Elsevier Science Ltd

Keywords: heterocyclic derivatives, polymethine dyes, IR spectrum region, absorption bands, synthesis and studies, spectral characteristics.

INTRODUCTION

The synthesis and study of the spectral characteristics of new polymethine dyes is of great importance for developing the theory of color of organic compounds, as well as for solving some practical problems in such areas as quantum electronics and the film industry, which particularly need stable polymethine dyes absorbing in the IR region and which have high intensity and selectivity.

One promising way for the creation of stable polymethine dyes absorbing in the IR region is the synthesis of appropriate new derivatives of nitrogen-

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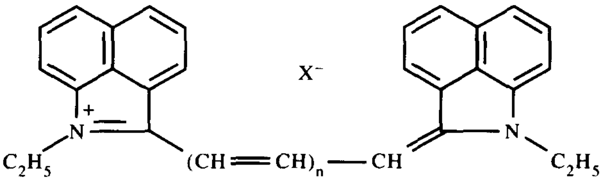
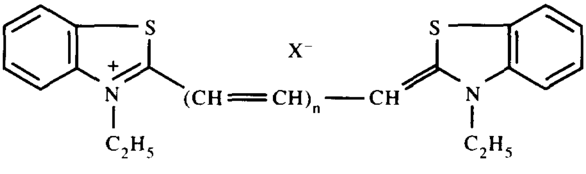
*Corresponding author.

containing heterocycles, which would then enable one to obtain deeply colored cyanine dyes with a short polymethine chromophore.

For example, dyes based on nitrogen-containing heterocycles, and which had a very long absorption wavelength, were obtained[1] from benzo[c,d]-indole derivatives, the length of the polymethine chain being the same.

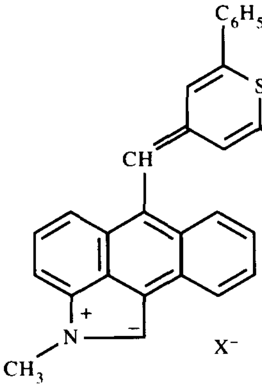
Analysis shows that the deepening in color in dyes of this type is due to cyclization effects of the pyrrole nucleus and to annelation of the aromatic ring. Thus, the trimethinecyanine **1b** has absorption maximum at 760 nm, i.e. bathochromically shifted more than 200 nm compared to the thiacyanine **2b** ($\lambda_{max} = 558$ nm),[2,3,4] a value which almost coincides with the absorption maximum of the thiatricarboncyanine **2d**. Because of these properties dyes of type **1** based on benzo[c,d]indole are widely used, for example, in quantum electronics.[5,6]





We have synthesized some new end heterocyclic residues, which are useful for obtaining deeply colored dyes, by annelation of the benzo[c,d]indole nucleus and by including part of the polymethine chain of this type of dye into a molecule of the condensed heterocycle. Thus, for example, based on pyrroloanthrone derivatives (which are of interest due to their intense luminescence in solution), we have synthesized dyes containing a nucleus of naphtho[1,2,3-c,d]indole and which are much more deeply colored than their analogues based on benzo[c,d]indole.

The monomethinecyanine dye **3**[7] has an absorption maximum of 788 nm, i.e. absorbing at longer wavelength than the corresponding trimethinecyanine dye **4** with a longer polymethine chain ($\lambda_{max} = 760$ nm). The data obtained suggested that new end heterocyclic groups of this type had great potential as reagents for the design of deeply colored dyes with a short polymethine chain.



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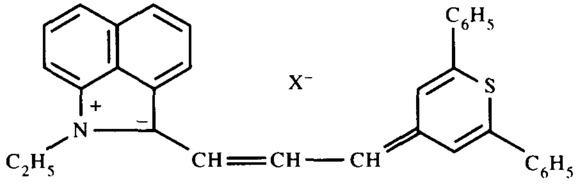

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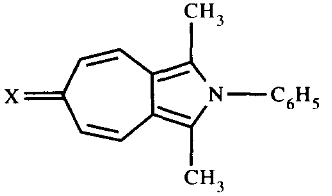
In order to synthesize new derivatives of nitrogen heterocycles containing a pyrrole nucleus condensed with an aromatic ring, we have studied transformations of substituted cyclohepta[c]pyrroles.

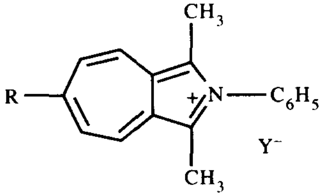
GENERAL EXPERIMENTAL

Reaction of the ketone **5**, obtained by the previously reported procedure,[8] with phosphorus pentasulfide led to the thione **6**,[9] which was then alkylated at the sulfur atom to form the corresponding methylthiosubstituted derivative **7**.[10]

5 $X{=}O$
6 $X{=}S$
7 $R = SCH_3$
8 $R = CH_3$
9 $R = CH{=}CHN(COCH_3)C_6H_5$



5, 6



7–9

Intermediates of type **8** were obtained by the reaction of 6-oxocyclohepta[c]pyrrole **5** with organometallic compounds. The salt of structure **8** can also be used as the initial product for the synthesis of corresponding electrophilic reagents; for example, the hemicyanines of type **9**, which are required for obtaining polymethine dyes by the usual methods in cyanine chemistry.

It should be noted that in contrast with the practically colorless 2-methyl- and 2-methylthiosubstituted derivatives of quaternary salts of conventional nitrogen-containing heterocyclic compounds used as reagents for synthesizing polymethine dyes, salts **7** and **8** are extremely deeply colored. Thus, their absorption maxima in acetonitrile are at 595 and 634 nm, respectively, i.e. in the region typical for thiacarbo- and thiadicarbocyanine dyes of type **2b** and **2c**. It was feasible to anticipate, therefore, significant spectral effects from dyes based on these reagents.

In this respect it was initially necessary to analyze the electronic structure and nature of the color of azoniaazulene derivatives.

DISCUSSION

As follows from the data for the distribution of the electron density in the model cation of azoniaazulene[8] and its isoelectronic structural analogue azulene[11] (long-wave maximum at 697 nm and the most intense maximum at 580 nm), the first electron transition responsible for the long wavelength absorption band is polarized along the symmetry axis of the molecule and is accompanied by the transfer of electron density from the seven-membered nucleus to the five-membered one.

Charge alternation similar to that in the polymethine chain of cyanine dyes is observed in these molecules. It should be noted that, according to the calculation data, introduction of electron-donor substitutents into either azulene or azoniaazulene in an even position should shift the absorption band to a shorter wavelength (for the former, this has been confirmed experimentally in many examples). This effect is illustrated by comparing the spectra of the methylthiosubstituted salt **7** with that of the methyl analogue **8**: the absorption maximum of the former is shifted to lower wavelength by 39 nm (Tables 1 and 2).

Creation of a polymethine dye based on azoniaazulene by binding of the polymethine chain with the second electron donor end-group to the carbon atom in the 6th position of the azoniaazulene nucleus results in the conjugated chain system. In this case the direction of the electron transition within the polymethine chain (as for the conjugation chain in the dye formed) is practically the same as that in the azoniaazulene nucleus.

TABLE 1

Spectral Parameters of the Compounds

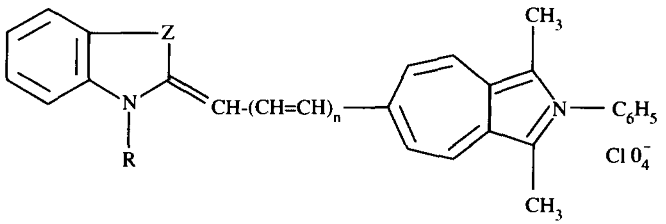
Dye	λ_{max}, *nm (log* ε) *B* CH_3CN
3	788 (4, 71)
4	760
7	595
8	634
10a	553 (4, 73)
10b	669 (4, 92), 620 (4, 85)
11a	694
12a	626 (4, 97)
12b	748 (5, 35)
12c	859
13a	710
13b	810 (5, 35)
15b	565 (4, 10)
16	676
17	638
18	696 (4, 95)
19	620 (4, 89)
20b	685 (5, 07), 638 (4, 91)
20c	784 (5, 00), 716 (4, 93)
24a	580 (4, 34), 460 (4, 04)
24b	685 (4, 85), 505 (4, 25)
25	617 (4, 84), 498 (4, 08)
26	564 (4, 53), 498 (4, 46)
27	558 (4, 84), 453 (4, 22)
33	793
34	830 (4, 56)
35	837

By convention, the molecules of such dyes may be considered as a system of two linear strongly interacting electron transitions (dipoles) (similar to the analysis of the spectral characteristics of biscyanine dyes containing two polymethine chromophores).[12] In this case, one (usually narrow) absorption band should be observed in the spectra of dyes based on the azoniaazulene nucleus, its position being determined by the nature of the two transitions. Where the electron transfers are directed to the same side of the molecule, the shift is bathochromic, and if they are directed to opposite sides, it is hypsochromic.

Thus, in our case the ability of the second end heterocyclic residue to localize the positive charge (i.e. to change the direction of electron transfer) seems to exert a considerable effect on the position of the absorption bands of the dyes with the azoniaazulene nucleus.

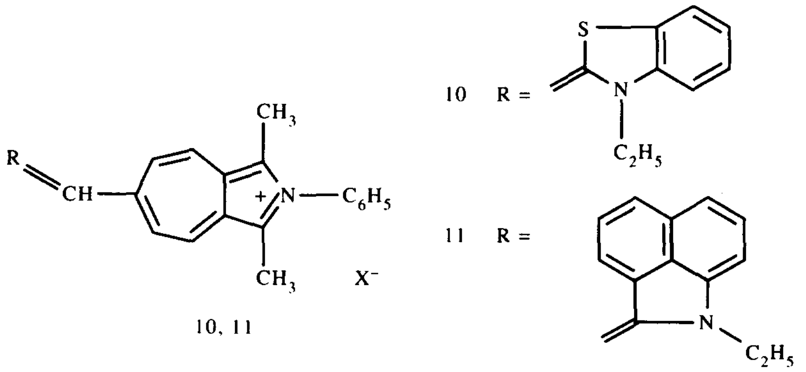
To investigate the influence of the structure of dyes based on azoniaazulene on their spectral characteristics, we synthesized a series of asymmetric

TABLE 2
Spectral Parameters of the Dyes



Dye	*X*	*R*	n	λ_{max}, *nm*				
				CH_3CN	C_2H_5OH	*DMFA*	C_6H_6	$C_6H_4Cl_2$
20b	$C(CH_3)_2$	CH_3	1	685,638	690, 642	693,643	697,645	710,660
20c	$C(CH_3)_2$	CH_3	2	784,716	789,725	790,718	791,730	814,759
10b	S	C_2H_5	1	669,620	679,626	680,630	688,642	704,652
19	CH=CH	C_2H_5	1	620	665,642	621	686	710
12b			1	748	752	757	763	770
13b			1	810	814	825	828	839

and symmetric dyes differing in both the length of the polymethine chain and in the nature of the end groups. A series of asymmetric monomethinecyanine dyes **10a**, **11a** were obtained by conventional procedures for the synthesis of cyanine dyes.



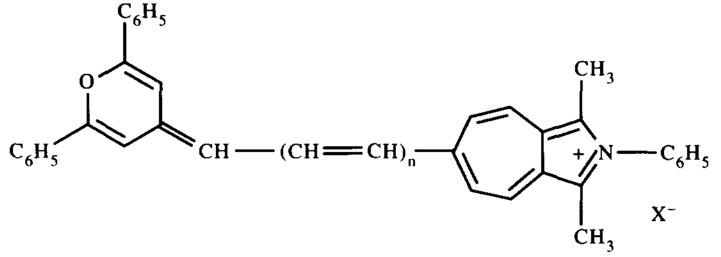
10, 11

The dyes based on azoniaazulene were found to have a deep color (Table 1); e.g. even the simplest thiamonomethinecyanine dye **10a**, although colored to some extent deeper than the corresponding initial azoniaazulene salts, absorbs at 553 nm, i.e. its absorption maximum is almost coincident with the absorption maximum of the symmetric thiatrimethinecyanine **2b**, the chromophore of which contains not one methine group, as in the case of dye **10a**, but three.

It should be noted that most of the atoms in the conjugated chain between the nitrogen atoms of the end heterocyclic residues of the dyes with azoniaazulene nucleus, i.e. the atoms on which the electron transition responsible for the long wavelength absorption band of the dyes **10a**, **11a** is localized, belong to the cyclohepta[c]pyrrole moiety.

Replacement of the benzothiazole nucleus in dye **10a** by heterocyclic residues having a larger effective length (i.e. by a parameter which determines an additional bathochromic shift of the long waveband caused by the end-groups) leads to a regular deepening in the color of the dyes. Thus, comparison of the thia- (**10a**) and the benzo[c,d]indole derivative (**11a**) shows a bathochromic shift of approximately 140 nm.

Extension of the polymethine chain of the dyes with an azoniaazulene nucleus by one vinylene group leads to regular color deepening. For example, the value of the first vinylene shift for dyes **12a–c** on progressing from a mono- (**12a**) to a trimethinecyanine system (**12b**) is 122 nm, whilst that of the second shift (progressing to the asymmetric pentamethinecyanine **12c** (λ_{max} = 859 nm) is 111 nm (Table 1).

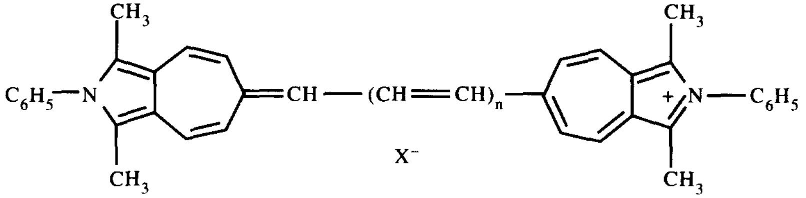


12a–c

a n = 0, b n = 1, c n = 2

As might be expected, the deep colour of the dyes with an azoniaazulene nucleus is typical not only for monomethines, but also for other derivatives with a longer polymethine chain.

We also synthesized the symmetric dyes **13a,b** based on the azoniaazulene salts **7–9**.



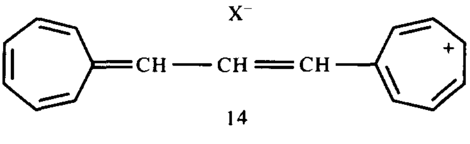
13a,b

a n = 0, b n = 1

The cyanines **13a** and **13b** are characterized by narrow absorption bands of high-intensity, the maxima of which are observed in the long wavelength region. It should be noted that the position of the absorption bands of both the asymmetric and symmetric dyes containing the azoniaazulene nucleus depends considerably on the nature of the solvent used for the spectrum measurements. Thus λ_{max} of the carbocyanine dye **13b** in acetonitrile is 810 nm, while in alcohol it is 814 nm. In solvents such as chloroform and dimethylformamide, it is observed at 828 nm, whereas in *o*-dichlorobenzene it is at 839 nm. This solvent influence seems to be due not only to solvent polarity, but also to solvation effects of the atoms of the polymethine chain and heterocyclic residue (Table 2).

At present, to the best of our knowledge, the cyanines **13a** and **13b** appear to be among the most deeply colored dyes within simple polymethine systems with the same polymethine chain length and which are based on nitrogen-containing heterocycles. It should be noted that on lengthening of the polymethine chain of the monomethinecyanine **13a** by one vinylene group (i.e. passing to the trimethinecyanine **13b**) the usual vinylene shift of the absorption maximum of 100 nm is observed, in common with most known symmetric cyanine dyes.

Comparison of the absorption maxima of the trimethinecyanine **13b** and its structural analogue **14** ($\lambda_{max} = 604$ nm) from the methyltropilium salt[13,14] shows that annelation of the tropilium and pyrrole nuclei leads to a considerable deepening in color ($\Delta\lambda = 206$ nm).



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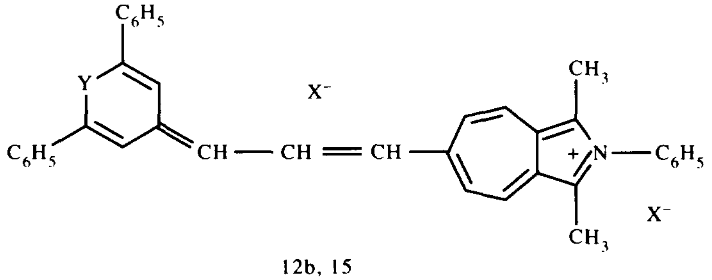
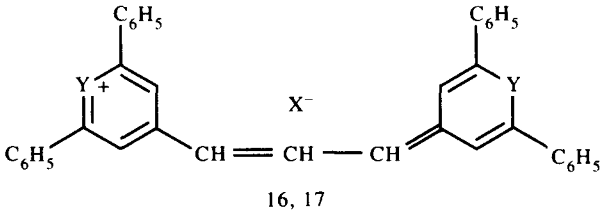
The spectral effect observed is most probably due to both lengthening of the conjugated chain and to an increase in the extent to which atoms of the end groups are involved in the electron transfer responsible for the long wave absorption of dyes based on cyclohepta[c]pyrrole heterocyclic residues.

The influence of the structure of the second end-group on the spectral characteristics of asymmetric dyes with an azoniaazulene nucleus is most conveniently illustrated by comparing the maxima of trimethinecyanines **12b** and its aza-anologue, dye **15**.



12b, 15

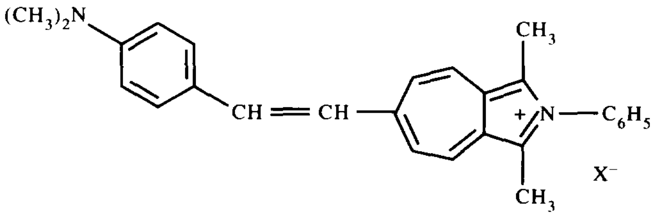


16, 17

12, 16 Y = 0, 15, 17 Y = NCH_3

As follows from this comparison, the position of the absorption maximum of asymmetric dyes depends on the electron-donor ability of this residue (i.e. its ability to localize the positive charge). Whilst the absorption maximum of the corresponding symmetric dyes based on pyrylium (**16** $\lambda_{max} = 676$ nm) and pyridine (**17** $\lambda_{max} = 638$ nm) are somewhat approximate, in the series of asymmetric dyes **12b** and **15** the much less intense maximum of the trimethinecyanine **15**, which contains the more electron donor pyridine nucleus, is observed in the lower wavelength region (565 nm).

Differences in the positions of the absorption maxima of the asymmetric dyes, compared to the corresponding symmetric derivatives, are usually due to the considerable electronic asymmetry of these dyes. Based on this approach, it is apparent that the azoniaazulene nucleus in the dyes can be characterized by a low electron-donor nature. Estimation of the electron-donor ability of the azoniaazulene nucleus by the deviation method ($\Delta\lambda$), based on values of the hypsochromic shifts of the absorption maxima observed for both dye **18** and the trimethinecyanines **19** indicates that the azoniaazulene nucleus is, in fact, of low basicity.



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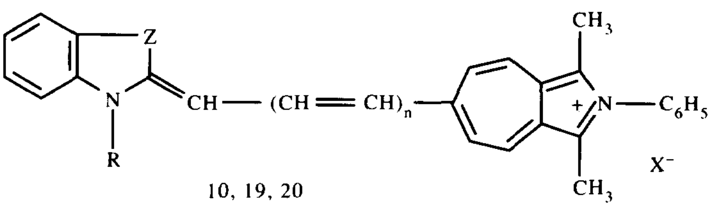


10, 19, 20

10b Z = S, 19 Z = CH = CH, 20 Z = $C(CH_3)_2$

It should be noted that while deeply colored dyes with the second low basic heterocyclic end-group, and their analogues with high basic heterocycles (Figs 1 and 2) each have one absorption band, two absorption maxima are observed in the spectra of derivatives of moderate basicity (Fig. 3). The ratio of the intensities of these bands changes with changes in the polarity of the solvent used. A similar phenomenon has been previously observed in studies of the absorption spectra of asymmetric pyrylocyanines,[15,16] and was explained in terms of both the large electron asymmetry of these dyes and of the solvent effect on bond equalization.

It is noteworthy that for acetonitrile solutions of the unsymmetrical azoniaazulene trimethinecyanines, the hypsochromic shift of the absorption band is the larger, and that of the shorter-wavelength band is the more intense, as the electron donor nature of the second heterocyclic end-nucleus increases.

It is important to note that solvatochromic effects are not typical for cations of polymethine dyes. But, in the case of dyes containing the azoniaazulene nucleus, not only are changes of the absorption band shapes observed, but also shifts of their maxima. For example, significant bathochromic shifts, and a decrease in the short wavelength (vibrational) band intensity, and of the halfbandwidth, are observed for dye solutions in acetonitrile compared with those in ethanol, benzene, and *o*-dichlorobenzene. These changes in the shape of and the maximum position of the absorbtion band occur with changes in the refractive index of the solvents.

The main characteristic feature of the azoniaazulene nucleus is a high symmetry of its molecule. Thus, most of the positively charged atoms of the heterocycle take part in the electron transition resulting in absorption in the visible and near-IR regions. It is probable that solvents of low polarity, and of a low ability for nucleophilic solvation, promote bond-order equalization of dye molecules derived from azoniaazulene both in the ground and exited states. Therefore very narrow and intense bands are observed in solvents such as benzene and *o*-dichlorobenzene. In contrast, in acetonitrile, which readily solvates the positively charged carbon atoms of the polymethine chain and the heterocyclic residues (especially the azoniaazulene moiety) residues, the specific solvation of the dye molecules in the ground state

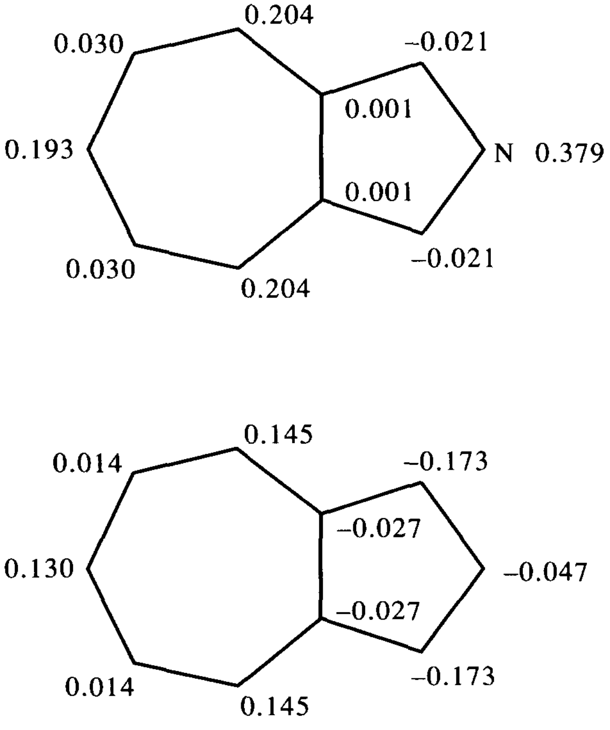


Fig. 1. Charge distribution on the atoms of model compounds.

results in a more pronounced distinction between the potential hypersurfaces of the two lowest energy single states, and hence leads to more probable transitions to vibrational sub-levels. For these reasons, broader bands and a more intense short-wavelength band are typical in solvents of this type.

The large hypsochromic shifts of dyes based on cycloheptapyrrole and a second highly basic heterocycle seem to be due not only to the effect of the electronic asymmetry of such molecules, but also to the additional effect of interactions between the electron transitions of the polymethine chain and with those of the cycloheptapyrrole nucleus (which in this case should lead to hypsochromic shifts). Comparison of the absorption maxima of the azoniaazulene salts, e.g. the salt **8** (λ_{max} 595 nm) and the symmetric dye **13a** obtained from it (λ_{max} 710 nm), with their structural analogues, namely, the isoelectronic analogue of azoniaazulene–azulene **21** (λ_{max} 580 nm)—and the corresponding symmetric monomethine analogue **22a** (λ_{max} 617 nm) based

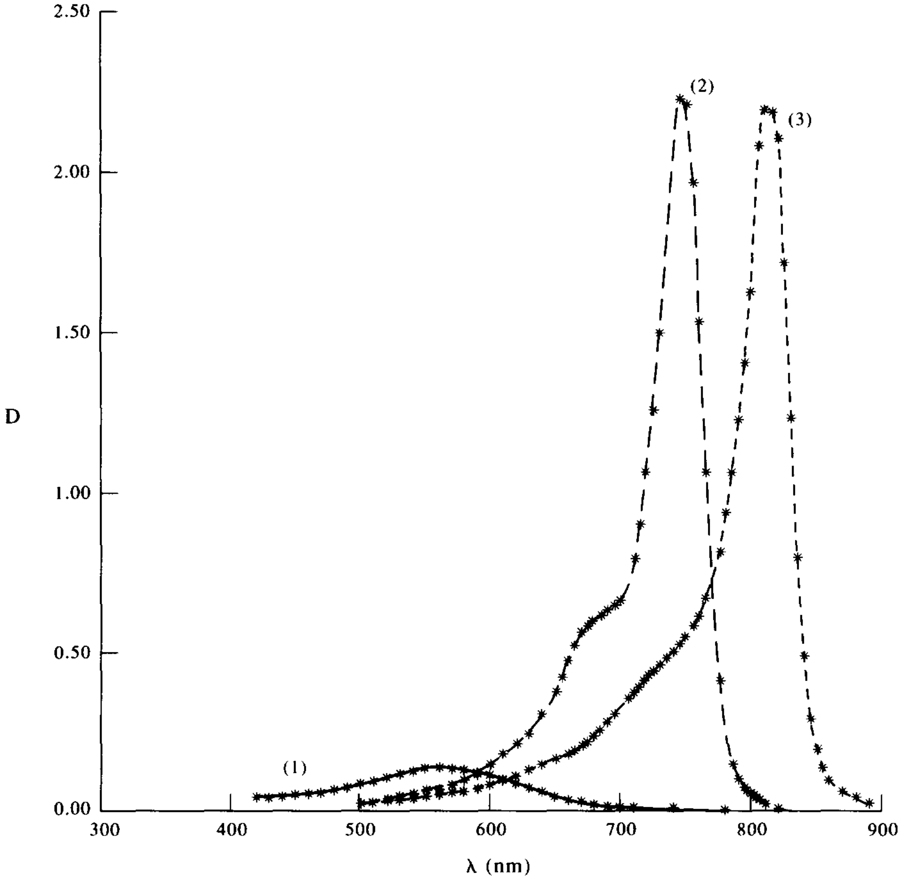


Fig. 2. Absorption spectra of dyes **15b** (1), **12b** (2), **13b** (3) in CH_3CN.

on it,[17,18] confirms the necessity of taking into account the interaction between the electron transition of the polymethine chain and that of the nucleus.

It should also be noted that, in contrast with the original end-groups of azulene and azoniaazulene, the dyes based on them are not isoelectronic analogues and, according to the previously noted classification,[19] belong to different classes in terms of electron symmetry. For these dyes, the transition of the polymethine chain and the inherent electron transition of the end-group, seem to be oppositely oriented. Moreover, replacement of one of the carbon atoms of the azulene moiety with the more electronegative nitrogen atom results in the involvement of the end residue in the electron transition responsible for the colour of dyes containing the azoniaazulene nucleus, and decreases the energy of the excited state; this, therefore, results in the dyes having a deep color.

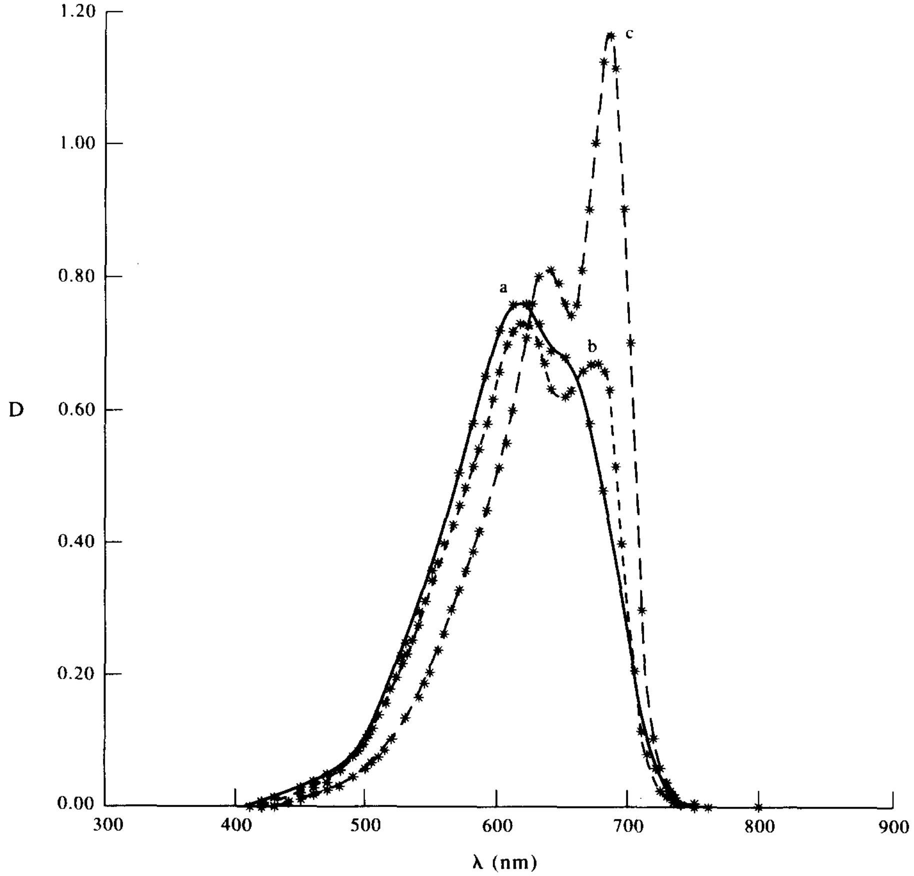
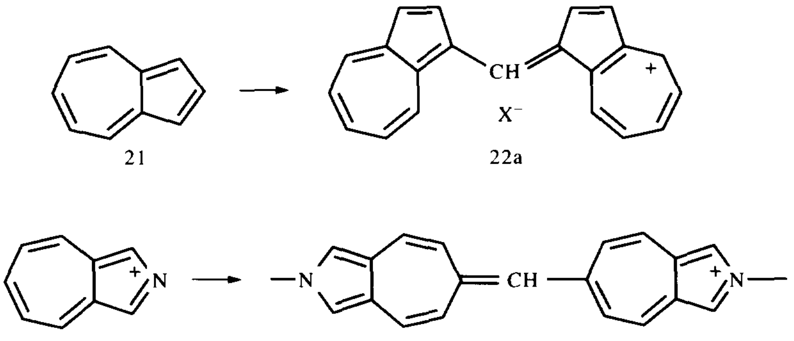


Fig. 3. Absorption spectra of dye **10b** in: CH_3CN (a), C_2H_5OH (b), o-$C_6H_4Cl_2$ (c).

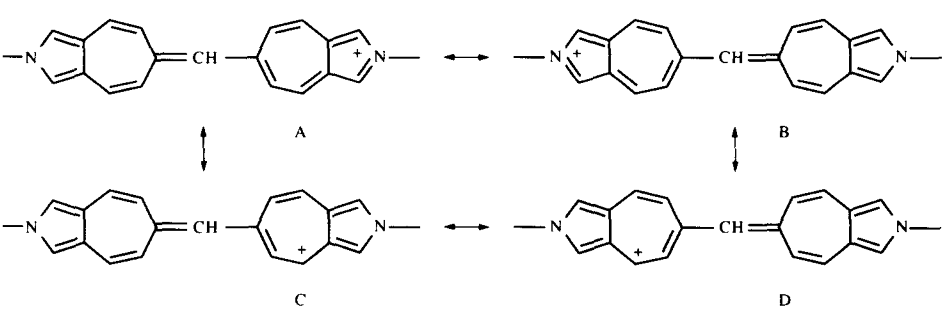
Within the scope of the valence band theory, the above observations imply that, in the case of dyes based on azoniaazulene, the major contribution to the color of dyes arises from mesomeric structures with the positive charge localized on the atoms of both the cycloheptene nucleus (mesomeric structures of type C, D) and the pyrrole nucleus (mesomeric structures A, B). This makes the conjugated system more extensive.

In contrast, in the case of dyes annelated to an azulene moiety, the positive charge is localized in the seven-membered ring, and the five-membered ring carries a negative charge. In this case the conjugated system is much shorter, and the color results from localization of the electron pair on the carbon atoms of the conjugated cyclopentene nucleus.

This approach (a simplified variant of configurational analysis), enables one to carry out an effectively aimed selection of structures which are promising for the construction of deeply colored dyes, and may also be used for the creation of new heterocycles for the synthesis of new types of polymethine dyes.

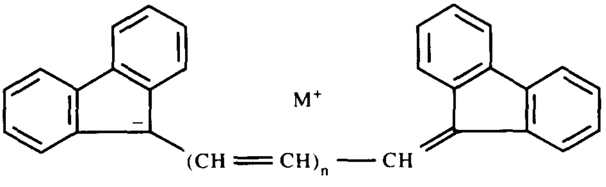


Scheme 1

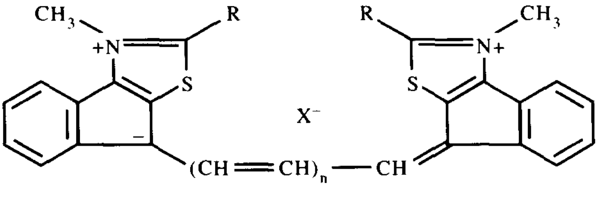


Scheme 2

Anionic dyes based on fluorene are known;[3,20] for example, the trimethinecyanine **23b** has an absorption maximum at 633 nm.[21]

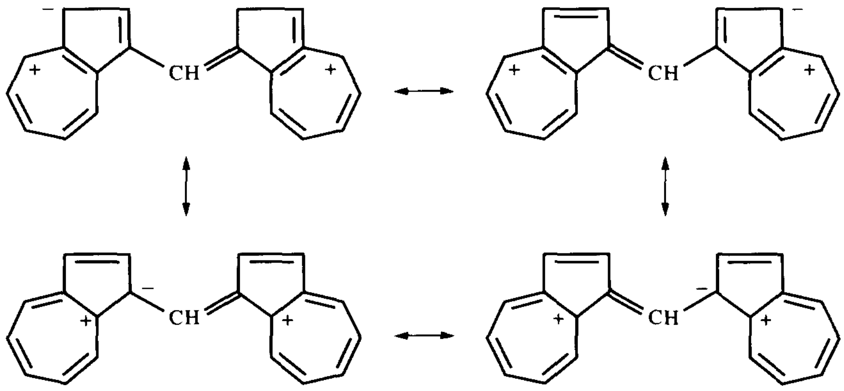


23a–c



24a–c

Since dyes of type **23** (unlike the corresponding azulene derivatives) are essentially anionic, an increase in the acceptor ability of the end group, which facilitates delocalization of the electron pair on the atoms of the end residue, should, in contrast, lead to a deepening in the color of such compounds.



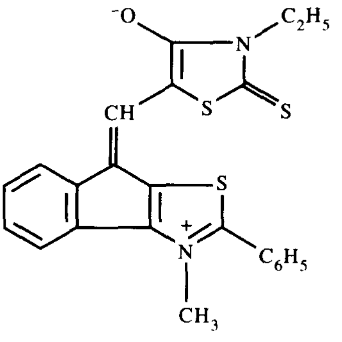
Scheme 3

Replacement of the benzene nucleus by the positively charged thiazolium nucleus results in noticeable deepening in the color of the corresponding dye **24** (this comparison of spectral characteristics being only approximate).

According to valence band theory, this indicates an increasing contribution of the mesomeric structures in which both positive and negative charges are localized within the thiazole nucleus.

It is of interest to note that the deeply colored cyanines **24** are cations, with a conjugation system typical to that of anionic dyes.

These factors determining the color of compounds of this type enable the construction of new polymethines. These may be both compounds containing a formal positive charge and a chromophore typical for merocyanines (for example, the dimethinecyanines **27**), and also formally neutral compounds (**25**,**26**) with a chromophore typical of anionic dyes.



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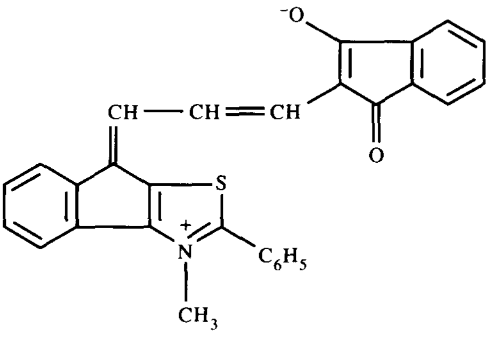

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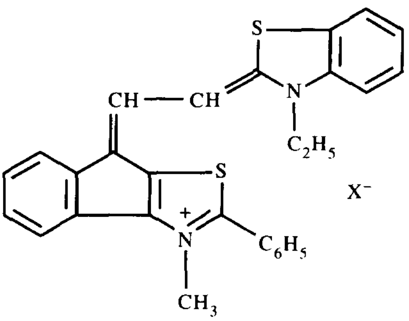
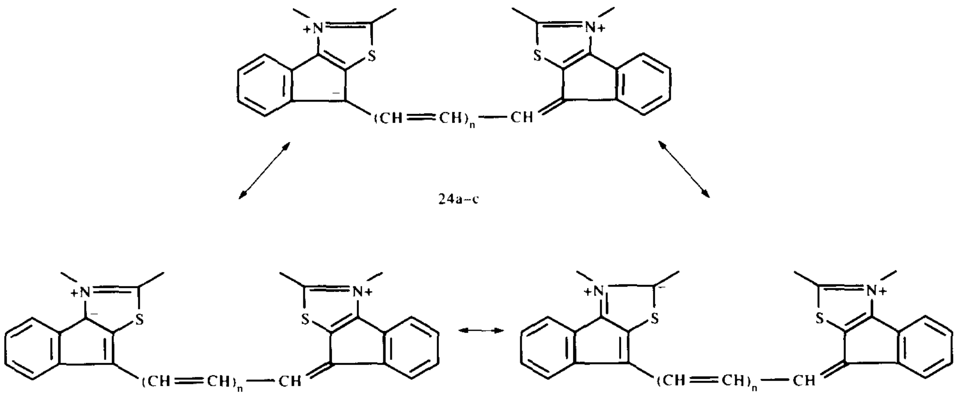


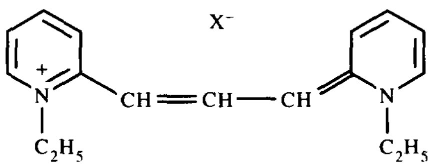
27

Such an approach to the development of new deeply colored dyes by modifying the nature of the end heterocycles may be successfully applied for heterocycles commonly used in the chemistry of polymethine dyes.

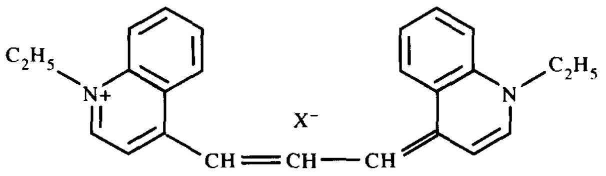


Scheme 4

For example, cyanines with pyridine or quinoline nuclei (especially lepidine derivatives) are know to be rather deeply colored. Thus, the absorption maxima of the carbocyanines **28** and **29**, which are derived from the quaternary salts of α-picoline, are 562 and 705 nm.[3,4]



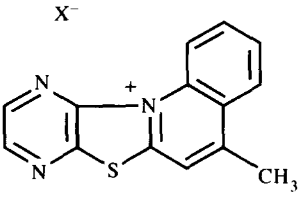
28



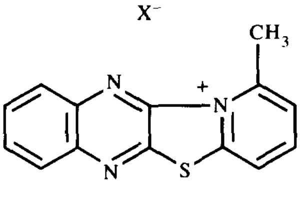
29

Addition of another heterocycle to the pyridine (quinoline) nucleus, thus facilitating delocalization of the electron pair on the atoms of this residue, should appreciably shift the absorption maxima of these dyes to the IR region.

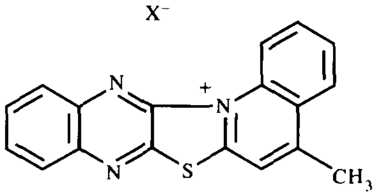
In this connection, we have also synthesized new heterocyclic systems, the molecules of which contain, besides pyridine or quinoline nuclei, residues of thiazolopyrazine or of thiazoloquinoxaline condensed with them.



30

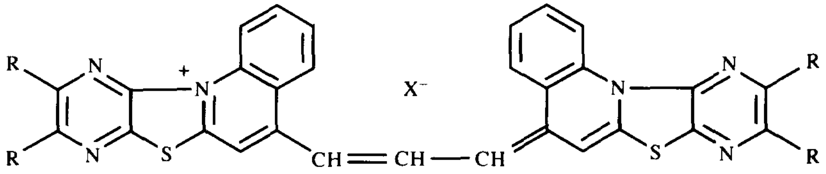


31

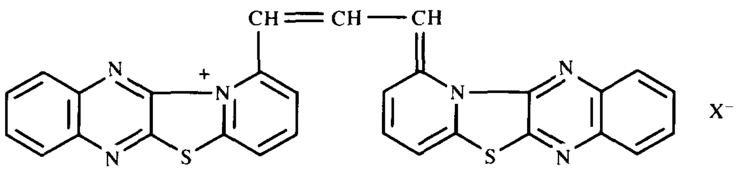


32

The synthesized methyl substituted salts of **30–32** react readily[22,23] with common electrophilic reagents used in the chemistry of polymethine dyes.



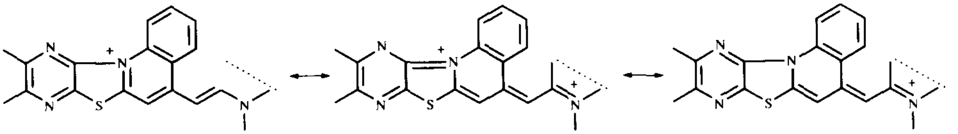
33 (R=H), 34 ($R+R = -(CH=CH)_2-$)



35

These compounds were found to possess a deep color, the absorption maxima of dyes based on both picoline and lepidine being similar.

The large shift in λ_{max} the longer wavelength of the dyes based on these new derivatives of pyridine and quinoline is also due to the fact that, with the addition of the electron-withdrawing nucleus of thiazoloazine, the contribution of mesomeric structures with localization of the negative charge on the end group (predominantly on the nitrogen atom) increases.



Scheme 5

This lengthens the conjugation chain, and favours stabilization of the excited state of the dyes, thus decreasing its energy level, i.e. causes a bathochromic shift of the absorption maximum. The energetics of the arrangement of the double bonds in the nuclei, and the strain in the heterocycle system account for the different effects on the spectral characteristics arising from condensation with a residue of either picoline or lepidine, as well as on the benzoannelation of the pyrazine nucleus.

Therefore, the considerable electron transition of a nucleus available in the dye, due to the additional annelated acceptor heterocycle (which coincides with the transition moment of polymethine chromophore in direction), results in an appreciable bathochromic shift of the absorption maxima of the corresponding dyes. Thus, for example, the carbocyanine dyes **34, 35** (830–837 nm) absorb at more than 100 nm longer wavelength than their lepidine analogues.

Based on these results, it can be concluded that the projected synthesis of new nitrogen-containing condensed heterocycles, by annelation of additional nuclei favouring delocalization of electron density from the polymethine chain to the heterocyclic residue, can result in the creation of deeply colored dyes with predicted properties.

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