POLYMETHINE DYES BASED ON 2-AZONIAAZULENE

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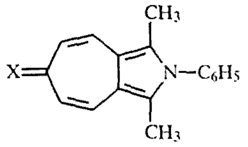
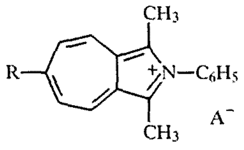
Previously unknown polymethine dyes of symmetrical and unsymmetrical structure based on cyclohepta[c]pyrrole were synthesized and their spectral properties investigated.

In order to obtain new polymethine dyes based on nitrogen-containing heterocyclic compounds we have examined the reactions of substituted cyclohepta[c]pyrrole derivatives.

By reacting ketone I, which was synthesized using a technique described in a previous work [1], with phosphorus pentasulfide, we obtained thione II, this being alkylated in the usual way at the sulfur atom [2, 3] to afford the corresponding derivative III.



I, II



III-V

I X = O, II X = S, III R = SCH_3, A = I, IV R = CH_3, A = ClO_4, V R = -CH = CHN($COCH_3$)C_6H_5, A = ClO_4

The well-known salt IV [1] was also used to synthesize the dyes and to obtain the corresponding hemicyanines of type V, which are employed as reagents for synthesizing polymethine dyes.

It is interesting to note that unlike the virtually colorless corresponding 2-methyl- and 2-methylthio-substituted quaternary salt derivatives of the nitrogen-containing heterocyclic compounds normally used to synthesize polymethine dyes, salts III and IV have very deep colors. Thus their absorption maxima in acetonitrile appear at 595 and 634 nm respectively, i.e. in the spectral region where carbo- and dicarbocyanine dyes absorb. Dyes based on cycloheptapyrrole could therefore be expected to have quite surprising spectral effects. Consequently it was essential to analyze, first and foremost, the electronic structure and coloring type of azoniaazulene derivatives. As can be deduced from data on the electron density distribution in the molecules of the azoniaazulene standard cation [1] and its isoelectronic structural analogue azulene [4] (longwave maximum at 697 nm, most intense longwave band maximum at 580 nm), the first electron transition, which produces the longwave absorption band, is polarized along the axis of symmetry of the molecule and is accompanied by the transfer or electron density from the 7-membered to the 5-membered ring.

Charge alternation similar to that seen in the polymethine chain of cyanine dyes was observed in the molecules. It is significant that according to computational data the introduction of electron-donor substituents at the even-numbered positions of the azulene or azoniaazulene molecule (in the latter case this was substantiated experimentally using several examples) should result in an enhancement of color in the compounds. The absorption maximum for methylthio-substituted salt III did indeed shift 95 nm further towards the shortwave part of the spectrum than that of the methyl analogue IV.

Organic Chemistry Institute, Ukrainian Academy of Sciences, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 193-198, February, 1994. Original article submitted November 30, 1993.

0009-3122/94/3002-0173$12.50 ©1994 Plenum Publishing Corporation

TABLE 1. Characteristics of Synthesized Compounds

Compound	Empirical formula	mp, °C	UV spectrum λ_{max}, nm (log ε), in CH_3CN	$\Delta\lambda^{2*}$, nm	Yield %
II	$C_{17}H_{15}NS$	212...214			47
III	$C_{18}H_{18}INS$	190...191	595		80
VIa	$C_{27}H_{25}IN_2S$	263...265	553 (4,73)		70
VIб	$C_{29}H_{27}ClN_2O_4S$	259...260	620 (4,85), 669 (4,82)	16	85
VIIa	$C_{31}H_{31}ClN_2O_4$	241...243	638 (4,91), 685 (5,07)	11	77
VIIб	$C_{33}H_{33}ClN_2O_4$	230...233	716 (4,93), 784 (5,00)		63
VIII	$C_{31}H_{29}ClN_2O_4$	242...244	620 (4,89)	87	90
IXa	$C_{35}H_{28}INO$	188...190	626 (4,97)		26
IXб	$C_{37}H_{30}ClNO_5$	255...257	748 (5,35)	5	74
IXc	$C_{39}H_{32}ClNO_5$	>270	859		70
Xб	$C_{38}H_{33}ClN_2O_4$	186...190	565 (4,10)	159	57
XIa	$C_{31}H_{27}IN_2 \cdot CH_3CN$	118...120	694		79
XIб	$C_{33}H_{29}ClN_2O_4$	220...225	781 (5,15)	5	72
XII	$C_{27}H_{28}ClN_2O_4$	251...255	696 (4,95)	11	47
XIIIa	$C_{35}H_{31}ClN_2O_4$	>270	710		68
XIIIб	$C_{37}H_{33}ClN_2O_4$	265...267	810 (5,35)		94

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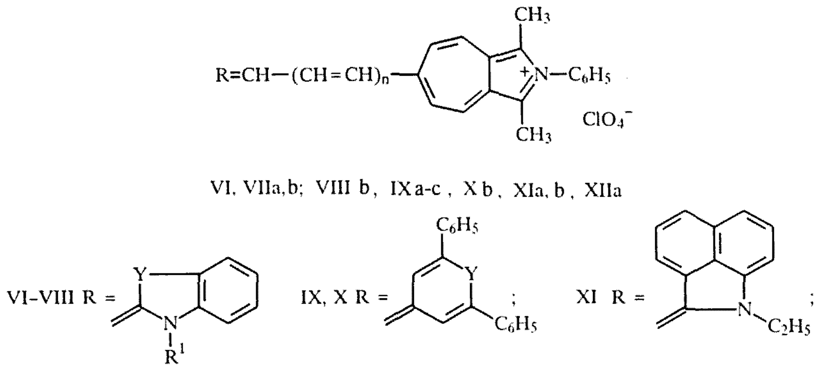
*Compound II was crystallized from toluene, compound VIa from pyridine, and the remaining compounds from acetonitrile.

2*Deviation value.

In order to study in detail the effect which the structure of azoniaazulene-based dyes has on their spectral characteristics, it was considered worthwhile synthesizing several symmetrical and unsymmetrical dyes having a characteristic polymethine chain length and end group structures.



XII R = $=CH\text{-}C_6H_5N(CH_3)_2$

VI—XII a n = 0, b n = 1, c n = 2; VI Y = S, $R^1 = C_2H_5$; VII Y = Me_2C, $R^1 = CH_3$; VIII Y = CH = CH, $R^1 = C_2H_5$; IX Y = O; X Y = NCH_3

Using the techniques normally employed in cyanine dye chemistry several unsymmetric mono-, tri- and pentamethinecyanine dyes were synthesized with the azoniaazulene ring (VI-XII). As can be seen from the data in Table 1, these azoniaazulene-based dyes have extremely deep colors. For example, even the simplest thiamonomethinecyanine dye VIa had an absorption band at 533 nm, i.e. its absorption maximum matched almost precisely that of the symmetrical thiatrimethinecyanine, whose chromophore contains not one (as in the case of monomethinecyanine VIa), but three methine groups.

It should be pointed out that most of the atoms in the conjugation chain between the atoms of the end heterocyclic fragments of azoniaazulene-based dyes (i.e., those atoms on which the electron transition responsible for the longwave absorption band of the dyes is localized) belong to the cyclohepta[c]pyrrole moiety.

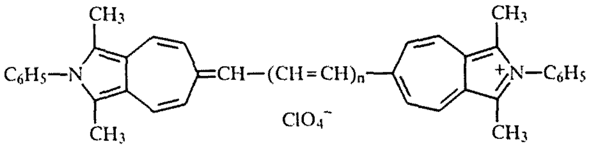
When the benzothiazole ring in the dye VIa was replaced by heterocyclic fragments of greater effective length (i.e. fragments for which the absorption maxima of the corresponding symmetrical dyes are shifted towards the longwave part of the spectrum), a regular increase in color intensity was observed. For example, the transition from compound VIa to benz[c,d]indole derivative XIa was accompanied by a bathochromic shift of ~140 nm.

When the polymethine chain in dyes IXa and XIa was lengthened by one vinylene group, a regular deepening of color resulted. For example, in the case of dyes XIa-c the first vinylene shift for the transition from mono- (a) to trimethinecyanine (b) was 122 nm, while the second (for transition to the unsymmetrical dicarbocyanine IXc, λ_{max} = 859 nm) measured 111 nm.

As can be seen from the data, the deep color of the dyes having the azoniaazulene ring was typical not just of the monomethines, but of corresponding derivatives having a longer polymethine chain.

It is interesting to note that while the deeply colored unsymmetric dyes IXb and XIb having a low-basicity second heterocyclic moiety and highly colored analogous having highly basic heterocyclic rings (e.g. quinocyanine VIIIb) possess one absorption band each, absorption bands with two maxima are observed in the spectra of derivatives with a medium-basicity second heterocyclic fragment (thia- and indocyanines VIb and VIIb). The ratio of the intensities of these bands varies with changing solvent polarity. At the same time there is also a significant change in absorption band half-widths. A similar phenomenon was observed previously during research on the absorption spectra of unsymmetrical pyrilocyanines [5]. It was interpreted in terms of the large electronic asymmetry of these dyes and the change in uniformity of the chromophore bonds when the solvent was varied.

Symmetrical dyes (XIIIa, b) were also successfully synthesized from azoniaazulene salts III-V (see Table 1).



XIIIa, b

Cyanines XIIIa and XIIIb have narrow high-intensity absorption bands, whose maxima are located in the longwave part of the spectrum. It is interesting to note that the position of the absorption bands for both symmetrical and unsymmetrical azoniaazulene-based dyes depends to quite an appreciable extent on the nature of the solvent used to measure the spectrum. Thus, the maximum for carbocyanine dye XIIIb measured 810 nm in acetonitrile and 814 nm in alcohol. In solvents such as chloroform and dimethylformamide the maximum was observed at 828 nm, and in o-dichlorobenzene at 839 nm. This effect probably stems not just from the polarity of the solvent, but the solvation of atoms in the polymethine chain and the heterocyclic moiety.

It would appear that cyanines XIIIa and XIIIb are the most deeply colored dyes of the known polymethines with the same polymethine chain length based on nitrogen-containing heterocyclic compounds. It should be noted that as in the case of symmetric dyes obtained from the heterocyclic moieties normally used in dye chemistry, when the polymethine chain of monomethinecyanine XIIIa was lengthened by one vinylene group (trimethinecyanine XIIIb), the normal 100 nm vinylene shift of the absorption maximum resulted.

It can be seen by comparing the absorption maxima of trimethinecyanine XIIIb and its structural analogue from the salt of methylpropylium (λ_{max} = 604 nm) [6, 7] that the transition to azoniaazulene derivatives produces an appreciable deepening in the color ($\Delta\lambda$ = 206 nm) of the dyes. Evidently, the observed spectral effect arises from the lengthening of the conjugation chain and the increased participation of end group atoms in the electron transition responsible for the longwave absorption of dyes during annelation of the tropyl and pyrrole rings.

The position of the absorption maxima of unsymmetrical dyes is usually determined both by the effective length of the heterocyclic fragment and its electron-donor capacity. The effect that the electron-donor capacity of the second end heterocyclic moiety has on the spectral characteristics of unsymmetrical azoniaazulene-based dyes is seen most vividly by comparing the maxima of pyrilo- (IXb) and pyrido- (Xb) trimethinecyanines. It follows from this comparison that the position of the absorption maxima of unsymmetrical dyes in this series is also significantly influenced by electron-donor capacity.

of the heterocyclic fragment that is conjugated with the azoniazzulene ring (i.e. the capacity to stabilize the positive charge on the latter). Indeed, while the maxima of the corresponding symmetrical trimethinecyanine dyes based on pyrilium (λ_{max} = 676 nm) and pyridine (λ_{max} = 638 nm) were quite similar, the maximum of the unsymmetrical trimethinecyanine Xb with the greater electron-donor capacity of its pyridine ring was observed in a much shorter wave region of the spectrum (565 nm) than that of the unsymmetrical dye IXb (748 nm) with its pyrilium ring.

These differences are usually caused by the potential electronic asymmetry of such cyanine molecules. It follows from this that the azoniaazulene ring in dyes is of low basicity. This conclusion was corroborated by assessing the electron–donor capacity of the azoniaazulene ring using the deviation method ($\Delta\lambda$) from the hypsochromic shift of the observed absorption maximum for styryl XIIa.

Nevertheless, the abnormally large hypsochromic shifts of the dyes synthesized from a cycloheptapyrrole ring and a second strongly basic heterocyclic ring probably stem not only from the significant electronic symmetry of these molecules, but also from the interaction of electron transitions in the polymethine ring and the inherent electron transition of the cycloheptapyrrole ring, which in this particular case should indeed produce hypsochromic shifts of the absorption maxima because of the opposite direction of electron transitions. It would appear that the extraordinarily high deviation of the unsymmetrical trimethinecyanine dye having a pyridine ring (Xb) can be explained in precisely these terms.

EXPERIMENTAL

Electronic spectra were recorded on a Specord M-40 spectrometer and PMR spectra were taken on Bruker WP-100 SY in $CDCl_3$, internal standard TMS.

Elemental analysis data for compounds II, III, and VI-XII with respect to C, N(S), and the halogen was in accordance with calculated values.

1,3-Dimethyl-2-phenyl-6H-cyclohepta[c]pyrrole-6-thione (II). A mixture of 2 g (8 mmoles) of ketone I and 4 g (18 mmoles) of P_2S_5 was kept for 2 h in 50 ml of dioxane at a temperature of 100 ± 5°C and then filtered. The filtrate was diluted with 200 ml water, and the resultant precipitate was filtered off and washed with water. PMR spectrum: 2.21 (6H, s, CH_3); 7.00 (2H, d, J = 11.5 Hz, 5- and 7-H); 7.20 (2H, m, o-H_{Ar}); 7.44 (2H, d, 4- and 8-H); 7.55 (3H, m, m-, p-H_{Ar}).

1,3-Dimethyl-6-methylthio-2-phenyl-cyclohepta[c]pyrrolium Iodide (III). A 0.4 g sample (2.8 mmoles) of methyl iodide was added to a solution of 0.56 g (2 mmoles) of thione II in 20 ml acetonitrile and the mixture was left at a temperature of 20-25°C for 72 h. The solution was filtered and evaporated to dryness in a water-jet pump vacuum. PMR spectrum: 2.61 (6H, s, CH_3); 2.93 (3H, s, SCH_3); 7.35 (2H, m, o-H_{Ar}); 7.52 (2H, d, J = 14 Hz, 5- and 7-H); 7.69 (3H, m, m-, p-H_{Ar}); 8.69 (2H, d, 4- and 8-H).

1,3-Dimethyl-2-phenyl-6-(2-acetanilidovinyl)cyclohepta[c]pyrrolium Perchlorate (V). A 0.2 g sample of ethylisoformanilide was added to a solution of 0.174 g (0.5 mmoles) of salt IV in 2 ml acetic anhydride. After boiling for 2 min and adding 0.02 g of dry sodium acetate, the mixture was kept for 5 min at 120°C. After cooling, the product was precipitated with ether. Yield 0.2 g (81%). λ_{max} = 471 nm (CH_3CN). Compound V was used without purification for synthesizing unsymmetrical dyes.

1,3-Dimethyl-6-[3-ethyl-2(3H)-benzothiazolylidene]methyl-2-phenylcyclohepta[c]pyrrolium Iodide (VIa). A mixture of 0.204 g (0.5 mmoles) of methylmercapto derivative III, 0.175 g (0.5 mmoles) of 2-methyl-3-ethylbenzothiazolium iodide and 0.1 ml of triethylamine was boiled for 15 min in 3 ml acetonitrile. After cooling to 0°C the dye precipitate was filtered off and washed with ether.

Unsymmetrical Carbocyanines (VIb, VIIb, IXb and XIb) (general method). A mixture of 0.5 mmoles of perchlorates IV and 0.5 mmoles of the corresponding β-hetarylacrolein was dissolved in 2 ml acetic anhydride and kept in the presence of 0.01 g dry sodium acetate for 10 min at 110°C. The dye was precipitated from solution using an excess of dry ether and washed with water (3 ml), isopropyl alcohol (5 ml) and ether after filtration.

Unsymmetrical Dicarbocyanines (VIIc, IXc) (general method). A mixture of 1 mmole of perchlorate IV, 1 mmole of the corresponding aldehyde, 4 ml of acetic anhydride, and 0.05 g of dry sodium acetate was kept for 10 min at 100°C. It was then treated as described above for carbocyanines VI, VII, IX, and XI.

1,3-Dimethyl-6-[3-(1-ethyl-2(1H)-quinolinylidene)]-1-propenyl-2-phenylcyclohepta[c]pyrrolium Iodide (VIII). A mixture of 0.2 g (0.4 mmoles) of derivative V, 0.135 g (0.4 mmoles) of 2-methyl-1-ethylquinolinium tosylate, 0.02 g of dry sodium acetate, and 2 ml of acetic anhydride was heated for 5 min. The dye was precipitated with ether and washed with water, isopropyl alcohol and ether.

1,3-Dimethyl-6-[2,6-diphenyl-4(4H)-pyranylidene]methyl-2-phenylcyclohepta[c]pyrrolium Iodide (IXa) was obtained in a similar way to dye VIa.

1,3-Dimethyl-6-{3-[1-methyl-2,6-diphenyl-4(4H)-pyridylilidene]}-1-propenyl-2-phenylcyclohepta[c]pyrrolium Perchlorate (X). A mixture of 0.3 g (0.5 mmoles) of dye IXb and 2 ml (5 mmoles) of 7.5% methanolic methylamine solution was boiled for 15 min. After cooling, the dye was precipitated by means of an aqueous sodium perchlorate solution. The product was purified by reprecipitation from acetonitrile using aqueous sodium perchlorate solution.

1,3-Dimethyl-6-[1-ethyl-2(3H)-benz[c,d]indolylidene]methyl-2-phenylcyclohepta[c]pyrrolium Iodide (XIa). A mixture of 0.174 g (0.5 mmoles) of salt IV, 0.180 g (0.5 mmoles) of 2-methylthio-1-ethylbenz[c,d]indolium iodide and 0.04 g of dry sodium acetate was boiled for 15 min in 10 ml acetonitrile. After cooling to 20 ± 5°C, the dye was precipitated by adding a solution of 0.2 g of sodium iodide in 20 ml water and washed with water and ether after filtration.

1,3-Dimethyl-6-(4-dimethylaminobenzylidene)-2-phenylcyclohepta[c]-pyrrolium Perchlorate (XII). A mixture of 0.174 g (0.5 mmoles) of salt IV, 0.075 g (0.5 mmoles) of p-dimethylaminobenzaldehyde and 2 ml of acetic anhydride was boiled for 5 min. After leaving for 2 h at 20-25°C, the reaction mixture was diluted with an equal volume of ether. The precipitate was filtered off and washed with ether.

1,3-Dimethyl-6-{1,3-dimethyl-2-phenyl-6(6H)-cyclohepta[c]-pyrrolylidene}methyl-2-phenylcyclohepta[c]pyrrolium Perchlorate (XIIIa). A mixture of 0.408 g (1 mmole) of salt III and 0.350 g (1 mmole) of salt IV, 0.08 g of dry sodium acetate, and 10 ml acetonitrile was boiled for 10 min. After cooling, the dye was precipitated by means of dry ether, filtered off and washed with water and ether.

1,3-Dimethyl-6-{3-(1,3-dimethyl-2-phenyl-6(6H)-cyclohepta[c]-pyrrolylidene)}-1-propenyl-2-phenylcyclohepta[c]-pyrrolium Perchlorate (XIIIb). After 1 ml of ethylorthoformiate and 0.08 g of dry sodium acetate had been added to a solution of 0.35 g (1 mmole) of salt IV and 4 ml of acetic anhydride, the mixture was boiled for 5 min. After cooling, the dye was precipitated with dry ether, filtered and washed with water and ether.

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