## PYRYLOCYANINES. 27.\* SYMMETRICAL POLYMETHINE DYES WITH AN INDENO[2,1-b]PYRYLIUM NUCLEUS

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# A number of symmetrical dyes with an indeno[2,1-b]pyrylium nucleus were synthesized. It is shown that the peculiarities of their absorption spectra are due to the specific characteristics of the condensed heteroring.

It is known that symmetrical polymethine dyes with a 4,6-diphenylpyrylium nucleus of the I type have significantly longer-wave absorption than virtually all analogous derivatives of different heterocycles [2]. Because of the fact that the carbon—carbon bonds of the heterocyclic residues in  $\alpha$ -pyrylocyanine dyes participate actively in the overall conjugation system, the introduction of dimethylene bridges that connect the  $\alpha$  positions of the polymethine chain with the  $\beta$  position of the pyrylium residues (dyes II) has a substantial effect on the color, leading to a significant bathochromic shift of the long-wave absorption band [3]. This effect is interpreted most simply within the framework of perturbation theory, according to which the magnitude and sign of the spectral effect will be determined by the mutual orientation of the interacting electron levels and the coefficients of the orbitals at the bonding sites. For pyrylocyanines of the II type the coefficients of the highest occupied molecular orbitals (HOMO) will have the highest absolute values at these sites. In the case of connection by an ethylene bridge, according to [4], the determining factor will be the repulsion of the HOMO of the dye from the antisymmetric filled level of the bridge. As a result, this connection leads to a decrease in the energy gap, which also explains the observed bathochromic shift of the long-wave absorption band.



According to the data in [5, 6], in the case of the formation of a ring due to an o-phenylene grouping that connects the same positions of the dye the interaction of its HOMO with the antisymmetric orbital from the pair of degenerate lowest vacant molecular orbitals (LVMO) of benzene should be most effective. Because of this interaction, the energy gap should increase, and, as a consequence of this, the color of the dye should be heightened. This is, in fact, observed in the symmetrical cyclization of the chromophore of carbo- [4] and tricarbocyanines [5], which are class B dyes according to the classification system in [6, 7].

Within the framework of a systematic study of pyrylocyanines it seemed of interest to synthesize analogs of dyes II that contain o-phenylene bridge groupings instead of ethylene bridge groupings, i.e., dyes with indeno[2,1-b]pyrylium (III) and indeno[2,1-b]pyran (IV) residues, and to investigate the extent to which the spectral principles presented above apply to them. The synthesis of such dyes is worthy of attention also because ring formation at the  $\alpha$  position of the polymethine chain increases the stabilities of pyrylocyanines [3, 7], which is important, since some of them are used as passive valves for lasers [8].



In connection with the fact that the spectral characteristics of cyanines depend substantially on the structure of the terminal groups, a study of the absorption spectra of dyes based on indenopyran derivatives may give information not only regarding the distribution of the electron density on the atoms of their molecules but also regarding the

\*See [1] for Communication 26.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 605-608, May, 1991. Original article submitted September 7, 1989; revision submitted August 28, 1990.

_	Empirical	mp,* °C	UV spectral parameters				
Com~			first band		second band		Yield,
pound	formula	17	$\lambda_1$ , nm	(1g ɛ <sub>1</sub> )	λ <sub>2</sub> , nm	(lg 22)	
Vb Vlb VIc VIIa VIIb VIIb VIIc	$\begin{array}{c} C_{27}H_{18}O_2\\ C_{29}H_{24}CIO_5N\\ C_{31}H_{26}CIO_5N\\ C_{49}H_{31}CIO_6\\ C_{51}H_{33}CIO_6\\ C_{53}H_{35}CIO_6\\ \end{array}$	$\begin{array}{c} 223 \dots 225 \\ 261 \dots 262 \\ 230 \dots 231 \\ 224 \dots 226 \\ 218 \dots 220 \\ 234 \dots 235 \end{array}$	568 575 620 747 818 916	(3.70) (4,11) (4,24) (4,17) (4,81) (4,95)	382 442 508 476 516 565	(4,55) (4,57) (4,61) (4,11) (4,35) (4,28)	$ \begin{array}{c c} 100 \\ 37 \\ 65 \\ 91 \\ 28 \\ 60 \\ \end{array} $

TABLE 1. Characteristics of the Synthesized	i Compounds
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\*Compound Vb was crystallized from ethanol, while the remaining compounds were crystallized from acetic anhydride.

conformation of the latter. Such information is especially interesting, since indenopyran derivatives constitute an extremely specific group of pseudoazulenes [9, 10].

Aldehyde Va, which is formed [11] in the formylation of benzoxalene IV [12], was used as the starting compound in the synthesis of a symmetrical monomethinecyanine. Let us note that an attempt to synthesize this dye in one step by condensation of pyrylium salt III with ethyl orthoformate was unsuccessful, just as in the case of 2,3-dimethylene-4,6diphenylpyrylium perchlorate [3].

The condensation of salt III with  $\beta$ -dimethylaminoacrolein or 1-(dimethylamino)-5-formyl-1,3-butadiene was used to synthesize salts VIb,c, the hydrolysis of which gave the corresponding aldehydes with a greater chain length (Vb, for example). Symmetrical dyes VIIa,b are formed by heating aldehydes Va,b with perchlorate III.



Tri- and pentamethinecyanines VIIb, c are experimentally simpler to obtain in one step by condensation of salt III with malonic or glutaconic aldehyde anil hydrochlorides.

In comparing the maxima of the long-wave absorption bands of dyes VIIa-c (see Table 1) with the corresponding characteristics of pyrylocyanines of the Ia,b and IIa-c type (800, 910; 865, 960, 1080 nm, respectively [2, 3] it is apparent that heightening of the color is observed in the case of introduction of an o-phenylene group and in the case of symmetrical cyclization of the chromophore in class B dyes. The hypsochromic shift for monomethinecyanine VIIa as compared with the shift of its structural analog Ia with an open polymethine chain is 53 nm, while the shift is 98 nm for trimethinecyanine VIIb as compared with Ib. A comparison of the absorption maxima of dyes VIIa-c and IIa-c leads to still greater differences: 118, 142, and 164 nm, respectively. In the series of dyes VIIa-c the first vinylene shift is only 71 nm, while the second value (98 nm) is close to the usual value of 100 nm [13]. All of these data indicate the existence in the cation of monomethinecyanine VIIa of significant steric interactions that disrupt the coplanarity of the molecule. This leads to both an additional bathochromic shift of the maximum and pronounced broadening of the band with a decrease in the molar absorption coefficient.

A similar regularity in the vinylene shifts is observed in a series of xanthylocyanines, which are structurally similar to dyes VII, and is explained by the same reason [14].

In examining the logarithms of the molar absorption coefficients in a series of carbo- (VIIa), dicarbo- (VIIb), and tricarbocyanines (VIIc) (see Table 1) it is apparent that the logarithm is anomalously low (4.17) for carbocyanine VIIa but is 0.91 lower than for carbocyanine IIa [3]. In [3] it was shown that the introduction of an ethylene bridge into the pyrylocyanine molecule does not cause disruption of its coplanarity and, as a consequence of this, does not lead to broadening of the band with a decrease in the molar absorption coefficient. On the other hand, the above-noted spectral peculiarities of cyanine VII attest to the existence in its molecule of a high degree of steric hindrance due to the o-phenylene groups. An examination of Dreiding's models shows that such groupings affect not only the coplanarity of the chromophore of monomethinecyanine VIIa but also the conformation of the phenyl groups in the

4 position of the heterocyclic fragments, disrupting their conjugation with the overall chromophoric system. To obtain approximate information regarding the conjugation of the phenyl groups in the 4 position of benzoxalenes we calculated the torsion angle ( $\theta$ ) of these substituents from the Braude formula presented in [15]:

$$\cos^2\theta = \varepsilon/\varepsilon_0$$

where  $\varepsilon$  is the molar extinction of the long-wave absorption band of cyanine VIIa, and  $\varepsilon_0$  is the molar extinction of cyanine IIa from [3].

The torsion angle obtained (69°) attests to a low energy of conjugation of the phenyl groups with the overall chromophoric system. This steric effect of o-phenylene groups, together with their electronic effect, undoubtedly makes a definite contribution to heightening of the color of the dyes.

It should be noted that a distinctive characteristic of the synthesized dyes is the presence presence of two bands of comparable intensity in the visible region of their absorption spectra; lengthening of the polymethine chain leads to a substantial increase in the absorption intensity of the long-wave band and an increase in the distance between the bands. Our next communication will be devoted to the elucidation of the nature of these bands.

#### EXPERIMENTAL

The electronic spectra of solutions in acetonitrile were recorded with an SF-20 spectrophotometer. The characteristics of the synthesized compounds are presented in Table 1.

The results of elementary analysis of Vb-VIIa-c for Cl, C, H, and N were in agreement with the calculated values. 2,4-Diphenyl-9-(2-formylvinyl)indeno[2,1-b]pyran (V). A 20-ml (1 mmole) sample of 2% NaOH solution was added to a solution of 0.5 g (1 mmole) of hemicyanine VIb in 40 ml of acetonitrile, and the mixture was maintained at 90°C for 30 min. It was then poured into 100 ml of water, and the product was removed by filtration, washed with ethanol, and crystallized.

**9-(3-Dimethylamino-2-propenylidene)-2,4-diphenyl-9H-indeno[2,1-b]pyrylium Perchlorate (VIb).** A mixture of 1.7 g (4 mmole) of perchlorate III, 1.0 g (10 mmole) of 3-dimethylaminoacrolein, and 15 ml of acetic anhydride was heated to the boiling point, after which heating was discontinued, and the reaction mixture was allowed to stand overnight. The precipitated product was removed by filtration, washed with ethanol and ether, and recrystallized.

9-(5-Dimethylamino-2,4-pentadienylidene)-2,4-diphenyl-9II-indeno[2,1-b]pyrylium Perchlorate (VIc). A mixture of 0.84 g (2 mmole) of perchlorate III, 0.25 g (2 mmole) of 4-dimethylamino-1-formyl-1,3-butadiene, and 3 ml of acetic anhydride was heated to the boiling point and then allowed to cool slowly. After cooling, the product was precipitated by means of ether, removed by filtration, washed with ether, and recrystallized.

2,4-Diphenyl-9-[(2,4-diphenylindeno[2,1-b]pyran-9-yl)methylene]-9H-indeno[2,1-b]pyrylium Perchlorate. A mixture of 0.17 g (0.4 mmole) of perchlorate III, 0.14 g (0.4 mmole) of aldehyde Va, 0.5 ml of acetic anhydride, and 0.5 ml of acetic acid was maintained at 100°C for 10 min, after which it was cooled and diluted with dry ether. The resulting product was removed by filtration and recrystallized.

2,4-Diphenyl-9-[3-(2,4-diphenylindeno[2,1-b]pyran-9-yl)-2-propenylidene]-9H-indeno[2,1-b]pyrylium Perchlorate (VIIb). A mixture of 0.21 g (0.5 mmole) of perchlorate III, 0.07 g (0.25 mmole) of malonic aldehyde dianil hydrochloride, 1 ml of acetic anhydride, and 1 ml of acetic acid was heated to the boiling point, after which 0.04 g (0.5 mmole) of anhydrous sodium acetate was added, and the mixture was allowed to cool. The precipitated dye was removed by filtration, washed with acetic acid and ether, and recrystallized.

2,4-Diphenyl-9-[5-(2,4-diphenylindeno[2,1-b]pyran-9-yl)-2,4-pentadienylidene]-9H-indeno[2,1-b]pyrylium Perchlorate (VIIc). A solution of 0.29 g (1 mmole) of glutaconic aldehyde dianil hydrochloride in 3 ml of acetic anhydride was added to a solution of 0.84 g (2 mmole) of perchlorate III in 3 ml of glacial acetic acid, and the mixture was heated to the boiling point. A 0.16-g (2 mmole) sample of anhydrous sodium acetate was added to the refluxing solution, and the mixture was refluxed for 1 min. It was then cooled, and the dye was removed by filtration and recrystallized.

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## REACTIONS OF 3-IODO-7-DIALKYLAMINOCOUMARINS WITH SECONDARY AMINES

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UDC 547.587.51

The reaction of 3-iodo-7-diethylaminocoumarin and 2,3,6,7-tetrahydro-10-iodo-1H,5H-quinolizino[9,9a,1-gh]coumarin with secondary amines (diethylamine, piperidine, morpholine, imidazole, and benzimidazole) leads to 4,7-diaminocoumarins. The corresponding 3-iodo-4-chloro-7-dialkylaminocoumarins under similar conditions give 3-iodo-4,7-diaminocoumarins. 4-Aminomethyl derivatives of coumarins are formed in the reactions of 3-iodo-4-methyl-7-diethylaminocoumarin and 2,3,6,7-tetrahydro-9-methyl-10-iodo-1H,5H-quinolizino[9,9a,1-gh]coumarin with these secondary amines.

The controversy regarding the transformation pathways of 3-halocoumarins [1-3], as well as other closely related compounds such as 3-nitro-4-halocoumarins [4], in reactions with nucleophiles currently continues in the literature. It is known [1] that the reaction of 3-halocoumarins with strong nucleophilic reagents, including amines, can lead, depending on the substituent in the 4 position, to the usual products of nucleophilic substitution or may be accompanied by contraction of the pyrone ring, which leads to benzofuran derivatives [2]. It is also known that the reaction of 3-bromo-4-methylcoumarin with secondary amines is accompanied by the elimination of a hydrogen halide and leads to the corresponding aminomethyl derivatives in addition to products of nucleophilic substitution at the sp<sup>2</sup> carbon atom [5].

To ascertain the specific character of analogous reactions in the 3-halo-7-aminocoumarin series [6] in the present research we studied the reaction of I-VI with a number of secondary amines, viz., diethylamine, piperidine, morpholine, imidazole, and benzimidazole.

The most efficient reactions were observed when I-VI were heated with excess amine in solution in DMF and DMSO or without a solvent. As a result, we found that the starting coumarins can be divided into three types with respect to nucleophilic reagents.

On heating for 4-6 h at 80-120°C in an excess ( $\geq 10$  equivalents) of the amine, I and II gave amino-substituted derivatives VII-XII in 60-80% yields (Table 1) (see scheme on next page).

Under similar conditions dihalo derivatives III and IV gave 3-iodo-4,7-diaminocoumarins XIII-XVI in high yields (see Table 1). Compounds XIII-XVI are rather unstable substances that are sensitive to the action of light and decompose appreciably during chromatographic separation on silica gel to give dehalogenation products VIII-X and XII.

In contrast to I-IV, coumarins V and VI were converted to 4-aminomethyl derivatives XVII-XXIII, the yields of which reached 60-70%, in reactions with the amines. A more detailed analysis of the compositions of the reaction

K. A. Timiryazev Moscow Agricultural Academy, Moscow 127550. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 609-618, May, 1991. Original article submitted January 25, 1990.