PYRYLOCYANINES.
28.* UNSYMMETRICAL PYRYLO-2-CYANINES BASED ON AN INDENO[2,1-b]PYRYLIUM SALT

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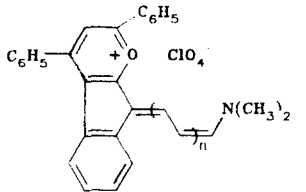
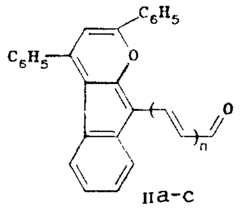
A number of unsymmetrical pyrylo-2-cyanines with an indeno[2,1-b]pyrylium ring were synthesized. It was established that their absorption spectra contain, in the visible region, two bands, the locations, intensities, and forms of which depend markedly on the nature of the second terminal group.

We have previously [1] described symmetrical pyrylo-2-cyanines in which the α positions of the polymethine chain are bonded with the β-carbon atoms of the heterocyclic residues by means of o-phenylene groupings, as well the production of hemicyanines Ib, c, the hydrolysis of which gives the corresponding aldehydes IIb, c.

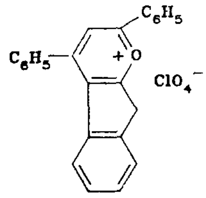

I a-c

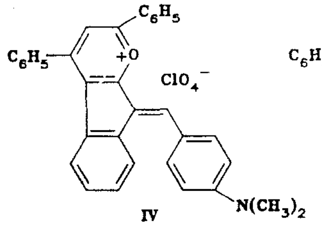

IIa-c

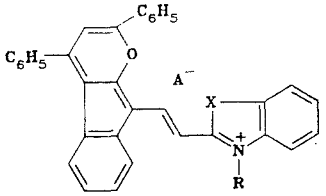
I, IIa n=0; b n=1; c n=2

For a detailed study of the effect of an o-phenylene bridge on the absorption spectra of pyrylocyanines, in the present research we synthesized a number of unsymmetrical pyrylo-2-cyanines from indeno[2,1-b]pyrylium salt III and aldehydes II.

Thus the reaction of perchlorate III with 4-dimethylaminobenzaldehyde or α-formylmethylene-1,3,3-trimethylindoline gave dyes IV and V:


III


IV


V-VIII

V $X=C(CH_3)_2$, $R=CH_3$, $A=ClO_4^-$; VI $X=O$, $R=C_2H_5$, $A=I^-$; VII $X=S$, $R=C_2H_5$, $A=I^-$; VIII $X=CH=CH$, $R=CH_3$, $A=ClO_4^-$

Unsymmetrical di- and tetramethinecyanines VI-IX, Xa, b, and XIa, b (see Table 1) were synthesized by condensation of aldehydes IIa, b with the corresponding quaternary salts of methyl-substituted heterocycles.

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*See [1] for Communication 27.

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	bp, °C*	λ_{max}, nm (log ε)**		$\lambda_1-\lambda_2$	$\varepsilon_1/\varepsilon_2$	Yield, %
			λ_1	λ_2			
Ib	$C_{29}H_{24}ClNO_5$	219...220	575 (4,11)	442 (4,57)	133	0,35	36
Ic	$C_{31}H_{26}ClNO_5$	230...231	620 (4,24)	508 (4,61)	112	0,43	65
IIa	$C_{25}H_{16}O_2$	177...179	510 (3,70)	396 (4,20)	114	0,32	50
IIb	$C_{27}H_{18}O_2$	203...205	568 (3,70)	382 (4,55)	186	0,14	100
IV	$C_{33}H_{26}ClNO_5$	>350	694 (4,27)	508 (3,97)	186	1,97	70
V	$C_{37}H_{30}ClNO_5$	280...281	629 (4,41)	489 (4,61)	140	0,63	50
VI	$C_{35}H_{26}INO_2$	262...263	599 (4,35)	466 (4,75)	133	0,39	80
VII	$C_{35}H_{26}INOS$	242...243	629 (4,28)	490 (4,56)	139	0,53	90
VIII	$C_{37}H_{28}ClNO_5$	284...285	623 (4,31)	503 (4,54)	120	0,59	80
IX	$C_{39}H_{28}F_4BNO$	307...308	740 (4,73)	565 (4,16)	185	3,69	74
Xa	$C_{43}H_{29}ClO_6$	333...334	707 (4,79)	540 (4,35)	167	2,79	62
Xb	$C_{45}H_{31}ClO_6$	220...222	806 (5,03)	603 (4,41)	203	4,12	100
XIa	$C_{36}H_{26}ClNO_5$	310...311	640 (4,30)	530 (4,44)	110	0,72	68
XIb	$C_{39}H_{30}ClNO_5$	283...284	657 (4,33)	574 (4,42)	83	0,81	21

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*The compounds were crystallized: IV, V, and VII-IX from acetic acid, VI from nitromethane, and Xa, b and XIa, b from acetic anhydride.

**Note that λ_1 is the first long-wave band, and λ_2 is the second short-wave band.

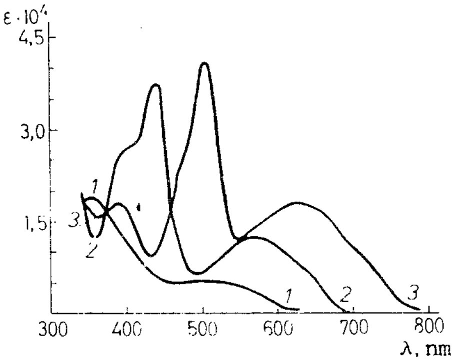


Fig. 1. Absorption spectra of solutions of the hemicyanines in acetonitrile: 1) Ia; 2) Ib; 3) Ic.

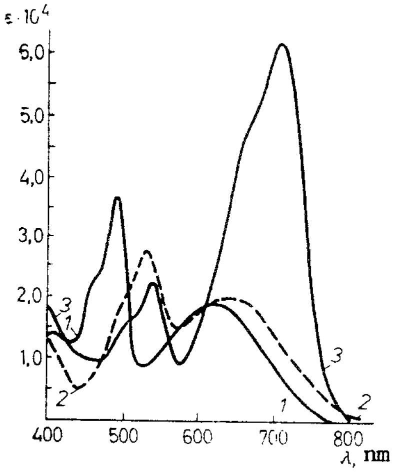
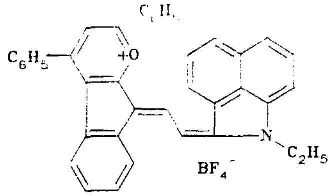
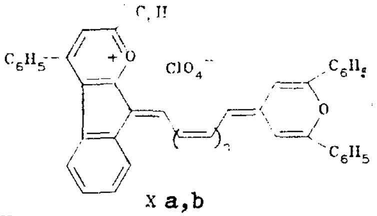


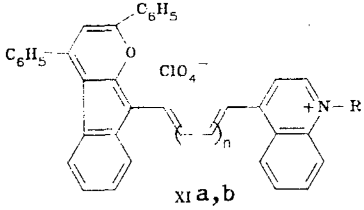
Fig. 2. Absorption spectra (in acetonitrile): 1) thiacyanine; 2) quino-4-cyanine; 3) pyrylo-4-cyanine.



IX



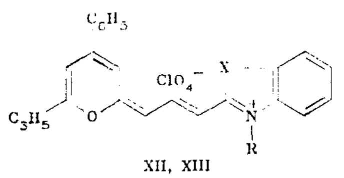
X a,b



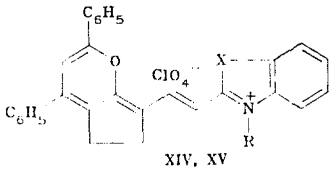
XI a,b

XI a n=0; b n=1

It is apparent from the data presented in Table 1 that the absorption spectra of the synthesized unsymmetrical cyanines, just as in the case of symmetrical dyes based on the indenopyrylium ring [1], contain, in the visible region, two bands of comparable intensity. When one compares the maxima of the long-wave absorption bands of unsymmetrical dyes V and VII (629, 629 nm) with the corresponding characteristics for their structural analogs — 4,6-diphenyl-2-methylpyrylium derivatives XII (682 nm) and XIII (708 nm) [2] and 4,6-diphenyl-2,3-trimethylene-pyrylium derivatives XIV (718 nm) and XV (724 nm) [3] — it is apparent that in the case of the unsymmetrical dyes, just as in the case of the symmetrical dyes [1], the introduction of an o-phenylene grouping, in contrast to an ethylene grouping, leads to a substantial shift of the absorption band to the short-wavelength region.



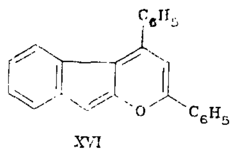
XII, XIII



XIV, XV

XII, XIV X=C$(CH_3)_2$, R=CH_3; XIII, XV X=S, R=C_2H_5

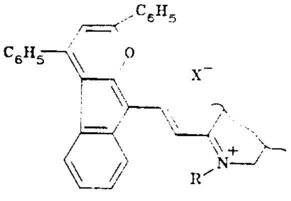
It should be noted that the locations and intensities of the two absorption bands depend on the electron-donor parameters (Φ_0) and the effective length (L) of the second terminal heteroring; one observes a rather distinct linear relationship between its L value and the location of the second absorption band. The relationship between the locations of the absorption maxima and the Φ_0 value of the second heteroresidue is less pronounced. Such spectral peculiarities of the synthesized unsymmetrical cyanines can evidently by explained by the different degrees of the effect of the electronic Φ_0 parameters and the L value of the second terminal heteroresidue on the locations of the first (long-wave) and second (short-wave) absorption bands. Higher intensity of the short-wave band than for the long-wave band is characteristic (see Fig. 1) for dyes that contain a heteroresidue with a small L value and a medium or large Φ_0 value (V-VIII and XIa, b). The same peculiarities of the absorption spectra are also observed for hemicyanines Ib, c. Their short-wave absorption bands (λ_2) are more intense than their long-wave bands (λ_1) (see Table 1 and Fig. 1), while both bands are shifted bathochromically with an increase in the length of the polymethine chain by one vinylene group; the short-wave band is shifted to a greater degree (λ_2 66 nm) than for the long-wave band (λ_1 45 nm). It should be noted that the form of the long-wave absorption bands of hemicyanines Ib, c is similar to that observed for benzoxalene (XVI); this may evidently indicate that they belong to this fragment.



XVI

On the other hand, the long-wave band is more intense for cyanines with heteroresidues that have small Φ_0 values and large L values (IV, IX, and Xa, b). As in the case of symmetrical cyanines [1], the intensity of the long-wave band and the distance between the maxima increase with an increase in the length of the polymethine chain of such dyes (for example, Xb) (see Fig. 2).

The effect of the electron-donor character of the second terminal heteroresidue on the absorption of light by unsymmetrical dyes with an indenopyrylium ring may evidently be due in part to the degree of their electron symmetry. The theoretical electron-donor character, expressed in degrees, for pyrylo-2-carbocyanine is 54.7° [2]. The introduction of an electron-acceptor bridge o-phenylene grouping should naturally lead to a decrease in the electron-donor character, and, therefore, if the Φ_0 value of the second terminal group will surpass in magnitude the Φ_0 value of the indenopyrylium ring, the contribution of the mesomeric structure (M) with localization of the positive charge on this group should increase.



M

The distribution of the electron density in the dye molecule in this case becomes appreciably less symmetrical, which leads to broadening of its absorption band and a decrease in its intensity [2, 3]. This sort of effect is also observed on passing from pyrylocyanine Xa to quinocyanine XIa. For the latter compound, the lepidine ring of which has greater electron-donor character, the long-wave band is actually broader and less intense than the λ_1 band for pyrylocyanine Xa (see Fig. 2).

In the case of unsymmetrical dyes in which the electron-donor character of the second terminal group is approximately the same, while the effective length differs markedly (for example, indo-, benz[c,d]indolo-, and pyrylo-4-carbocyanines V, IX, and Xa, respectively) one also observes great differences in the spectra. The low L value of the indolenine ring, as in the case of dye V, leads to an increase in the intensity of the short-wave band. On the other hand, the large L values for pyrylocyanine Xa and benz[c,d]indolocyanine IX leads not only to a sharp increase in the intensity of the long-wave band but also to its significant bathochromic shift (see Table 1).

The presence in the visible region of the absorption spectra of polymethine dyes constructed from condensed heterocycles of two bands has also been observed earlier. Thus in the case of dyes based on a thiazolo[3,4-*a*]pyrimidinium salt [4] and mesoionic thiazolo[3,2-*a*]pyrimidinium 3-oxides [5] it has been established that this sort of character of the spectra is due to two interacting electron transitions, one of which is localized on the atoms of the polymethine chain, while the second is localized on the atoms of the condensed heteroring; in the latter case it was demonstrated for the first time that the transition that is localized not on the polymethine, as is usually the case, but rather on the mesoionic fragment makes a greater contribution to the long-wave absorption band [5]. This sort of effect can probably also be used to explain some unusual principles in the absorption spectra of different types of polymethine dyes, as, for example, in the dibenzoxanthylocyanine series and in a number of isomeric (with respect to them) compounds [6, 7], which are structurally similar to dyes based on indenopyrylium salts; a specific property of pyrylocyanines, by virtue of their chemical structure, is the participation of a large number of heteroring carbon atoms in the electron transition responsible for the long-wave absorption band. Moreover, whereas in the case of pyrylo-2-cyanines the moment of the transition localized on the ring virtually coincides with the direction of the polymethine chromophore, the introduction of an o-phenylene bridge (compounds of the indeno[2,1-b]pyrylium series) not only increases the number of heteroring carbon atoms that participate in the transition but also evidently changes the direction of the transition in the ring. Since the ratio of the intensities of the absorption bands of biscyanines depends markedly on the angle formed by the vectors of the electron transitions [8], it may be assumed that the pronounced differences in these values observed for unsymmetrical cyanines with an indenopyrylium ring (for example, 0.39 for dye VI and 3.69 for IX) are due to a change in precisely these angles.

Thus we have synthesized unsymmetrical polymethine dyes, a characteristic peculiarity of which is the presence in the visible region of the absorption spectra of two bands; the electronic character of the second heteroresidue has a pronounced effect on the behavior of their maxima.

EXPERIMENTAL

The electronic spectra of solutions of the compounds in acetonitrile were recorded with an SF-20 spectrophotometer. The results of elementary analysis for C, H, Cl, F, I, and N for the new compounds were in agreement with the calculated values.

9-(4-Dimethylamino)benzylidene-2,4-diphenyl-9H-indeno[2,1-b]pyrylium Perchlorate (IV). A mixture of 0.18 g (0.4 mmole) of salt III, 0.08 g (0.6 mmole) of 4-dimethylaminobenzaldehyde, 1 ml of acetic anhydride, and 1 ml of acetic acid was heated at 100°C for 10 min, after which it was cooled, and the precipitated dye was removed by filtration and crystallized. A similar method was used to synthesize V-IX, Xa, b, and XIa, b.

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SPECTRAL-LUMINESCENCE PROPERTIES AND ACID-BASE PROPERTIES OF LUMINOPHORES OBTAINED FROM 3-IODO-7-DIALKYLAMINOCOUMARINS

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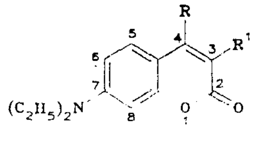
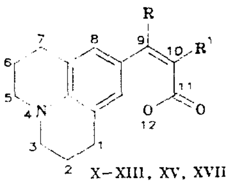
The absorption and fluorescence spectra of the conjugate acids of 7-dialkylaminocoumarins were studied, and their pK_a^I, pK_a^{II}, *and* pK_a^* *values were determined. It was established with the aid of PMR data that the primary protonation generally involves the nitrogen-containing substituent in the 3 or 4 position, while the secondary protonation involves the nitrogen atom in the 7 position.*

The spectral-luminescence and acid-base characteristics of a series of 7-aminocoumarins with a mono- or dialkylamino group in the 4 position were described in [1]. We have recently [2] reported the synthesis of new 7-aminocoumarin dyes I-XIII as a result of reactions of 3-iodo-7-dialkylaminocoumarins with secondary amines. In the present publication we discuss the absorption and fluorescence spectra and the pK_a values of the conjugate acids of I-XIII to ascertain the effect on these properties of a heteroaromatic substituent in the 4 position (in the 9 position for julolidine derivatives X-XIII, XV, and XVII) (coumarins I, II, X), of a dialkylamino group in the 3(10) position (coumarins VIII, IX, and XIII), and of the same substituents but bonded to the $C_{(4)}$ [$C_{(9)}$] atom by a methylene link (III-VII, XI, XII). As models for comparison we used the known coumarins XIV-XVIII [3, 4].



I-IX, XIV, XVI, XVIII



X-XIII, XV, XVII

I, X R = **N-imidazolyl** II R = **N-benzimidazolyl** III R = $CH_2N(C_2H_5)_2$; IV R = $CH_2N(CH_2)_5$; V, XI R = $CH_2N(CH_2CH_2)_2O$; VI, XII R = CH_2-**N-imidazolyl**; VII R = CH_2–**N-benzimidazolyl**, VIII, IX, XIII, XVI—XVIII R = CH_3; XIV, XV R = H; I—VII, X—XII, XIV—XVII R^1 = H; VIII $R^1 = N(CH_2)_5$; IX, XIII $R^1 = N(CH_2CH_2)_2O$; XVIII $R^1 = NH_2$

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