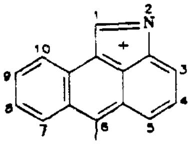
POLYMETHINE DYES BASED ON PYRROLOANTHRONE

Y. L. Briks, A. D. Kachkovskii, and N. N. Romanov UDC 547.819.45'759.31:541.651

Pyrroloanthrone has been used as the starting material in the synthesis of 6-methylthionaphthindolinium salts that were used in turn to obtain polymethine dyes. The dependence of the color of the cyanines on their chemical structure has been analyzed.

Currently, quantum electronics and motion picture photography have a special need for polymethine (PM) dyes that absorb in the near-infrared and have colors with high intensity and selectivity. The absorption bands of cyanine dyes can be shifted toward longer wavelengths [1] by lengthening the PM chain or by using as end-groups certain heterocycles with a large effective length (L) [2]. In a series of symmetric PM dyes, the introduction of one additional vinylene group into the chromophore usually shifts the maximum bathochromically by about 100 nm. However, this also lowers the stability of the dyes. Hence it appears promising to synthesize new, deeply colored PM dyes with a short PM chain. In turn, a systematic search must be made for heterocycles to be used in the synthesis of new cyanines with predetermined parameters.

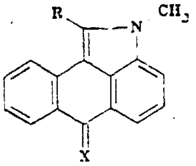
Among the available nitrogen-containing heterocycles being used as endgroups of PM dyes, the greatest effective length (L = 6.5) is that of the nucleus of benz[c,d]indole (absorption maxima of the carbocyanines and dicarbocyanines are 750 and 850 nm [3]). The value of L for the heterogroup is defined as the equivalent number of vinylene groups in terms of their influence on the chromaticity of the cyanines; this value can be estimated by quantum-chemical methods [2, 4, 5]. Calculations have shown that a substantial increase in the parameter L of this nucleus can be achieved by its annelation. Thus, for naphthindole (I) with the PM chain in position 6, L = 7.2; and the electron donor strength Φ = 27° [2, 4].



I

In light of this background, the present work has been aimed at developing methods for obtaining previously unknown dyes of this type and analyzing their absorption spectra. As starting materials we used the pyrroloanthrones IIa, b; the synthesis and certain reactions of these compounds have been studied in detail in [6, 7]. The heightened interest in such compounds can be attributed to their intense luminescence in solution. We have investigated the possibility of using this heterocyclic system as end-groups in PM dyes.

It was found that the aciton of phosphorus pentasulfide on compounds IIa, b gives their thioanalogs IIIa, b.



II-III a,b

II, III a R=H, b R=$COOCH_3$; II X=O, III X=S

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1413-1420, October, 1990. Original article submitted November 28, 1988.

TABLE 1. Characteristics of Compounds III-VIII

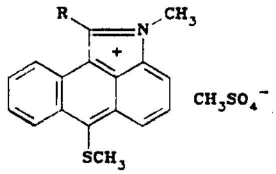
Compound	Empirical formula	T_{mp}, °C*	λ_{max}, nm ($\varepsilon \cdot 10^{-4}$)	Yield, %
IIIa	$C_{16}H_9NS$	182...186	321 (0,95) 339 (1,10) 544 (1,71)	80
IIIb	$C_{18}H_{13}NO_2S$	158...161	310 (0,80) 339 (0,87) 525 (0,89)	56
IVa	$C_{18}H_{17}NO_4S_2$	115...117	543	86
V	$C_{19}H_{11}N_3$	275	333 (1,10) 520 (1,75)	62
VI	$C_{26}H_{21}ClN_2O_4S$	255...257	333 (1,26) 592 (1,71)	55
VIIa	$C_{34}H_{24}ClNO_5$	234...236	376 (1,63) 748 (4,13)	57
VIIb	$C_{36}H_{26}ClNO_7$	220...222	350 (1,02) 716 (3,52)	37
VIII	$C_{34}H_{24}ClNO_4S$	242...245	384 (1,62) 788 (5,11)	34

---

*Compounds were crystallized as follows: IIIa from dioxane; IIIb from aqueous dioxane; V from DMFA; VI from a mixture of i-PrOH and CH_3CN; VIIa, b and VIII from CH_3COOH.

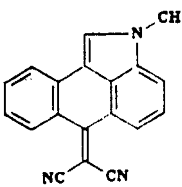
The purified products are quite deeply colored; their compositions and structures are confirmed by elemental analyses (Table 1) and the ^1H NMR spectroscopy (Table 2). It is interesting to note in the ^1H NMR spectra that, owing to the shielding effect of the sulfur atom, the signals of the protons lying close to the sulfur (in positions 7 and 5) are shifted downfield.

Through alkylation of the thiones IIIa, b by dimethyl sulfate, we obtained 6-methylthio-substituted salts of naphthindole IV, which are readily hydrolyzed to form the pyrroloanthrones II.

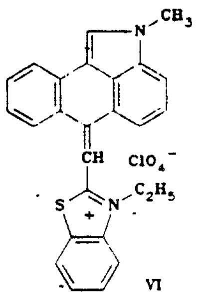


IV a,b

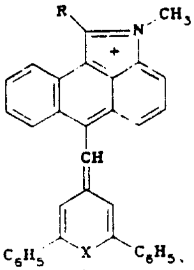
Further studies showed that, similar to the known α-alkylthio derivatives of quaternary salts of nitrogen heterocycles, compounds IVa, b interact readily with the appropriate nucleophilic intermediates that are commonly used in the chemistry of polymethine dyes. For example, upon interaction with the dinitrile of malonic acid, we obtained the merocyanine V; with a 2-methylbenzothiazolium salt, or with 4-methyl-2,6-diphenylpyrylium perchlorate or the corresponding thiopyrylium perchlorate, we obtain the monomethinecyanines VI-VIII.



V



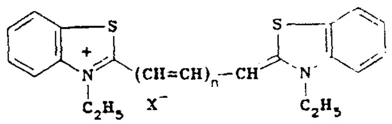
VI



VIIa, bVIII

VII a X=O, R=H; VII ' X=O, R=COOCH3; VIII X=S, R=H

The structures of the synthesized dyes were confirmed by their ^1H NMR spectra (Table 2). Upon comparison of the long-wave absorption maximum of the dye VI with that of the ordinary thiamonomethinecyanine IX (422 nm [8]), it is evident that the naphthindole nucleus does actually have a greater effective length, thus giving a substantial bathochromic shift (170 nm) when the change is made from the benzothiazole nucleus to the naphthindole nucleus.



IX, X

IX n=0; X n=1

A solution of the dye VI absorbs in the same region of the spectrum as do solutions of cyanines with a greater length of the chromophore. For example, the absorption maximum for the thiatrimethinecyanine X is only 558 nm [8].

Naturally, the replacement of the benzothiazole nucleus (L = 3.06) in the molecule of the thiamonomethinecyanine VI by a heterogroup with a greater effective length [pyrylium VIIa (L = 6.06) or thiopyrylium VIII (L = 7.23)] will lead to an additional regular bathochromic shift of the absorption maximum (156 and 196 nm). It is significant that these structural changes also give basic changes in the shape of the absorption curves (Fig. 1). For the pyrylomonomethinecyanine VIIa, the curve is narrower and more intense in comparison with the benzothiazole analog VI. However, the change in form of the absorption curves for solutoins of the cyanine dyes is related mainly to the presence of steric hindrance in their molecules, or to their electronic asymmetry.

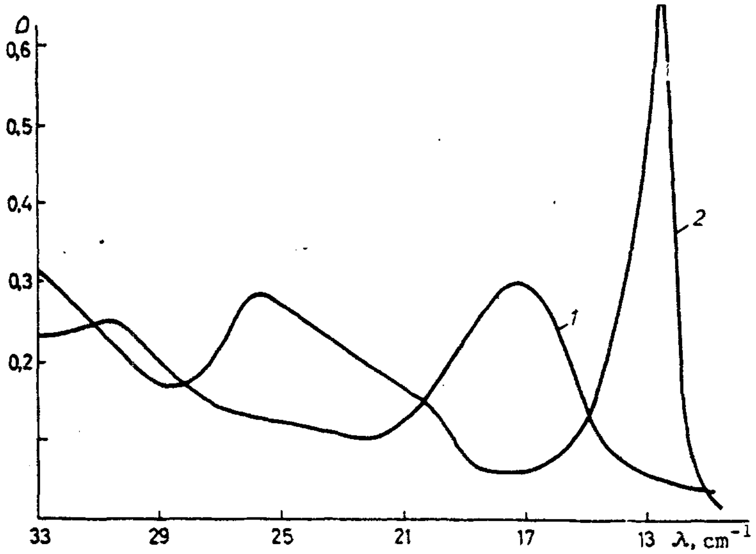


Fig. 1. Absorption spectra of dyes based on naphthindole: 1) dye VI; 2) dye VIIa (c = $2 \cdot 10^{-5}$ M).

TABLE 2. ^{1}H NMR Spectra of Compounds III-VI

Compound	Chemical shift δ, ppm (and J, Hz)
IIIa	8,86 (1H, d, 7-H, $J=8$); 8,54 (1H, s, 1-H); 8,30 (1H, d, 5-H, $J=8$); 8,08 (1H, d, 10-H, $J=8$); 8,05 (1H, d, 3-H, $J=8$); 7,76 (1H, dt, 9-H, $J=8,1$); 7,53 (1H, t, 4-H, $J=8$); 7,42 (1H, dt, 8-H, $J=8,1$); 4,01 (1H, s, N—CH_3)
IIIb	8,75 (1H, d, 7-H, $J=8$); 8,37 (1H, d, 5-H, $J=8$); 8,18 (1H, d, 10-H, $J=8$); 8,03 (1H, d, 3-H, $J=8$); 7,75 (1H, dt, 9-H, $J=8,1$); 7,52 (1H, t, 4-H, $J=8$); 7,45 (1H, dt, 8-H, $J=8,1$); 4,09 (3H, s, N—CH_3); 3,94 (3H, s, O—CH_3)
IVa	8,32 (1H, s, 1-H); 8,3...7,3 (7H, m, Ar-H); 3,99 (3H, s, N—CH_3); 3,38 (3H, c, S—CH_3)
V	8,57 (1H, d, 7-H, $J=8$); 8,52 (1H, s, 1-H); 8,2...7,3 (6H, s, Ar-H); 4,03 (3H, c, N—CH_3)
VI	8,38 (1H, c, 1-H); 8,3...7,3 (12H, m, Ar-H); 4,97 (2H, q, N—CH_2, $J=8$); 4,00 (3H, c, N—CH_3); 1,59 (3H, t, N—CH_2—CH_3, $J=8$)

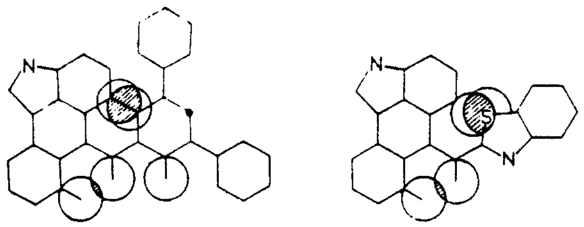


Fig. 2. Projection models of dyes VI and VIIa. Here and in Figs. 3 and 4, the shaded areas are those for which the electron density is increased by excitation; the unshaded areas are those for which the electron density is decreased by excitation.

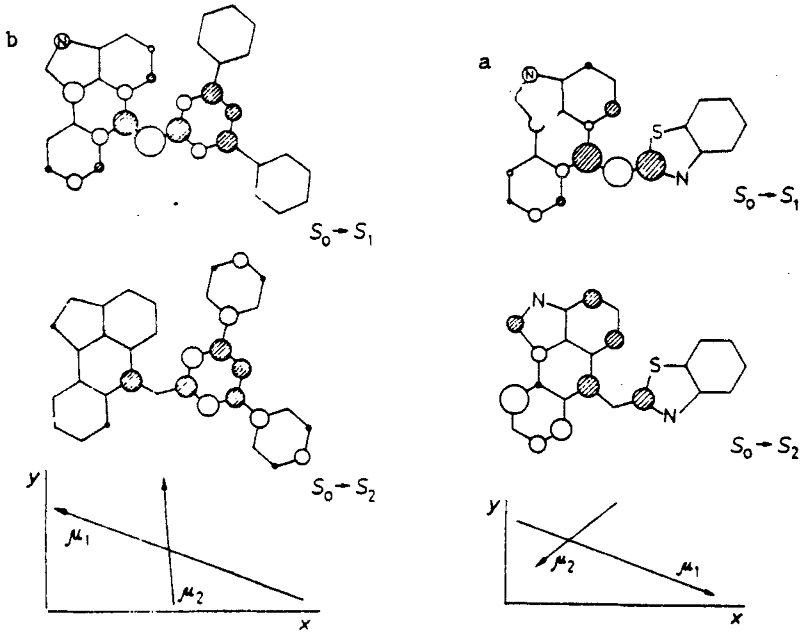
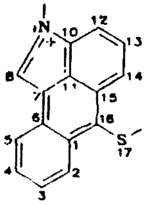


Fig. 3. Diagram of electron density redistribution upon excitation, and direction of transition moments, for dyes VI (A) and VIIa (B).

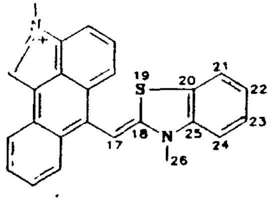
Steric hindrance in molecules of symmetric dyes leads to a bathochromic shift of the maximum and a broadening of the absorption band [9]. For asymmetric dyes, we may also observe hypsochromic shifts, depending on the order of the bond around which the fragments of the molecules rotate, eliminating the steric hindrance. From projection models of the cations VI and VIIa (Fig. 2), these projections having taken into account the bond angles, covalent radii, and radii of action of the atoms [10], it can be seen that the steric hindrance is on the same order of magnitude in these two molecules. An increase in the electronic asymmetry of cyanine molecules (with other conditions equal) leads to a hypsochromic shift of the absorption and maximum, along with a decrease in band intensity and an increase in band width [8]. In our case as well, apparently, in the series of dyes containing the low-basicity naphthindole nucleus (low-basicity as determined by quantum-chemical evaluation), the replacement of the low-basicity pyrylium group (Φ = 44°) by the more basic benzothiazole (Φ = 47°) does actually increase the asymmetry of the cyanine VI. This is reflected in the increase in width of the dye absorption band.

A feature of the absorption spectra of the dyes based on naphthindole is the presence of short-wave absorption bands as well, with intensities comparable to those of the long-wave bands. In order to interpret the observed spectra correctly and to determine localization of the electronic transitions, we have carried out quantum-chemical calculations of the electron density distribution in the ground and excited states in cations of the cyanines VI and VIIa and the methylthionaphthylindolinium IV (Table 3). These calculations indicate that the long-wave absorption band of the dye solution corresponds to a low-energy transition with a large moment of the transition, polarized from one nucleus to the other (Fig. 3). The directions of these transitions are opposite for the thio- (VI) and pyrylocyanines (VIIa). The second transiton has a lower energy and a smaller moment.

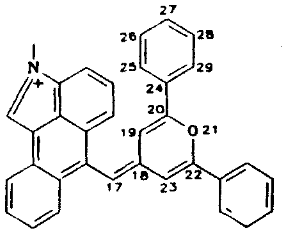
TABLE 3., Charge Distribution on Atoms of Compounds IV, VI, and VII in the Ground State (S_0) and in the First (S_1) and Second (S_2) Singlet Excited States*



IV



VI



VII

	S_0^{IV}	S_1^{IV}	S_2^{IV}	S_0^{VI}	S_1^{VI}	S_2^{VI}	S_0^{VII}	S_1^{VII}	S_2^{VII}
1	−0.045	−0,030	−0,009	−0,040	+0,007	−0.024	−0,034	+0,021	−0,032
2	+0,046	+0,107	+0,002	+0,030	−0,011	+0,175	+0,013	−0,013	+0,006
3	+0,024	+0,138	+0,049	+0,011	+0,062	+0,067	+0,004	+0,042	+0,004
4	+0,083	+0,032	+0,073	+0,057	+0,029	+0,058	+0,045	+0,028	+0,032
5	−0,001	+0,157	+0,003	−0,003	+0,025	+0,193	−0,005	+0,008	−0,006
6	+0,061	+0,034	+0,026	+0,041	+0,039	+0,007	+0,037	+0,038	+0,022
7	−0,086	+0,064	−0,085	−0,089	−0,006	−0,034	−0.090	−0.013	−0,090
8	+0,076	+0,018	+0,023	+0,039	+0,037	−0,024	+0,020	+0,036	+0,001
9	+0.399	+0,452	+0,385	+0,377	+0,420	+0,386	+0,370	+0,413	+0,366
10	−0,062	−0,054	+0,042	−0,051	−0,045	−0,046	−0,050	−0,050	−0,050
11	−0.041	−0,030	+0,185	−0.040	−0,053	−0,039	−0,042	−0,053	−0,048
12	+0,091	−0,015	−0,019	+0,047	+0,015	−0,030	+0,030	+0,009	+0,034
13	+0,014	+0,025	+0,225	−0,06	+0,014	−0,003	−0,009	+0,016	−0,009
14	+0,082	−0,045	+0,041	+0,002	−0,072	−0,089	+0,019	−0,008	−0,009
15	−0,041	−0,013	−0,0001	−0.024	+0,020	−0,022	−0,019	+0,039	−0,018
16	+0,199	−0,037	−0,065	+0,139	−0,069	−0,027	+0.122	−0,096	+0,026
17	+0,194	+0,198	+0,130	−0,121	+0.042	−0,110	−0,090	+0,140	−0,074
18				+0,104	−0,076	−0,039	+0,116	−0,028	−0,036
19				+0,225	+0,229	+0.198	−0,035	+0,012	+0,072
20				−0,040	−0,001	+0.001	+0,101	+0,019	+0,013
21				+0,001	−0,004	−0,002	+0,252	+0.214	+0,178
22				+0,028	+0,045	+0,062	+0,101	+0,025	+0,006
23				+0,027	+0,049	+0.064	−0,030	+0,008	+0,092
24				−0,019	−0,032	−0.029	−0,047	−0,042	+0,029
25				−0,062	−0,024	−0.013	+0,014	+0,003	+0,017
26				+0.363	+0,363	+0,323	+0,020	+0.020	+0,037
27							+0,050	+0,043	+0,104
28							+0,018	+0,019	+0,034
29							+0.025	+0.009	+0,028

---

*The charges on the atoms of phenyl ring 2 of dye VIIa are practically the same as on the equivalent atoms of ring I (within 0.001).

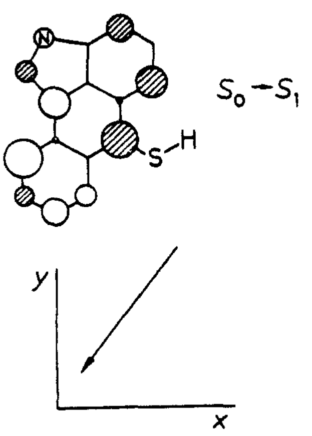


Fig. 4. Diagram of electron density distribution upon excitation, and direction of transition moment, for 6-methylthio-substituted salt of naphthindole IVa.

For a graphic analysis of localization of transitions, diagrams are constructed for the distribution of electron density on the atoms of dye cations. As can be seen from Fig. 3, in the dye molecules, the first electronic $\pi-\pi^*$ transition ($S_0 \rightarrow S_1$) is accompanied by a considerable change in electron density on the atoms of the polymethine chromophore. This sort of picture is typical for the first transition in PM dyes, which is responsible for their long-wave absorption bands. Thus, the first band in the dyes based on naphthindole corresponds to the polymethine chromophore. The second transition is localized mainly on one of the heterocyclic end-groups: on the naphthindole nucleus for the thiacyanine VI, and on the pyrylium nucleus for the pyrrolocyanine VIIa. The diagram of electron density distribution in the second transition ($S_0 \rightarrow S_2$) for dye VI is reminiscent of the diagram for the cation of IV ($S_0 \rightarrow S_1$) (Fig. 4). The influence of the benzothiazole nucleus shows up only in a small transfer of charge to the carbon atom in position 2 of this end-group (i.e., in the vinylog position relative to the naphthindole nucleus). Consequently, in the second $\pi-\pi^*$ electronic transition, the PM chain can be regarded as a conjugated substituent of the actual chromophore of the naphthindole nucleus. In the molecule of the cation of the monomethinecyanine VIIa, the change in electron density in the second transition already takes place in the pyrylium nucleus with the participation of only the carbon atom in position 6 of the naphthindole.

Since both transitions are localized on exactly the same atoms, they can interact with each other. As is known from the theory of interaction of polymethine chromophores in a series of biscyanines [9], it is manifested in a shift of the positions of the absorption band maxima of the "parent" dyes and a change in their intensity ratio. Here, the bathochromic shift of the long-wave band and the hypsochromic shift of the shorter-wave band (movement of the bands away from each other) will be greater for closer values of the energy of the chromophores. In this case, the ratio of intensities for the bands of these interacting transitions is determined by the angle between the directions of the chromophores; the interaction is the greatest for chromophores with parallel directions, whereas perpendicular chromophores do not interact.

As can be seen from Fig. 3, for the thiacyanine VI, the moments of the ($S_0 \rightarrow S_1$) and ($S_0 \rightarrow S_2$) transitions (with a certain degree of approximation, they can be compared to the transition energy) differ considerably, and the angle between them is obtuse. Consequently, the bathochromic shift of the long-wave band should be small, and the intensity should be lowered. For the dye VIIa, in contrast, the moments are comparable in magnitude, and the angle between them is acute. Consequently, as a result of the interaction of the polymethine chromophore and the true chromophore of the nucleus, the long-wave absorption band should be shifted bathochromically to a greater degree, and its intensity should be increased.

Thus, it has been shown that derivatives of pyrroloanthrone can be used for the synthesis of deeply colored dyes with a short polymethine chain.

EXPERIMENTAL

The calculations of L and Φ_0 were performed by a procedure given in [2] with the following parameters for the heteroatoms: $\alpha_N = \alpha + \beta$, $\alpha_O = \alpha + 2\beta$, $\alpha_S = \alpha + 0.7\beta$; $\beta_{CN} = \beta$, $\beta_{CO} = 0.8\beta$, $\beta_{CS} = 0.4\beta$.

The electronic spectra were recorded on a Specord M-40 spectrophotometer (in acetonitrile); the ^1H NMR spectra were recorded on a Bruker WP-100SY spectrometer (in DMSO-D_6). Internal standard TMS.

2-Methyl-2,6-dihydronaphth[1,2;3-c,d]indole-6-thione (IIIa). A mixture of 1.2 g (5 mmoles) of N-methylpyrroloanthrone IIa and 2.2 g (10 mmoles) of phosphorus pentasulfide in 40 ml of dioxane was refluxed for 15 min; the residue was filtered off and refluxed twice with dioxane. The hot filtrate was diluted with water. The precipitate was filtered off.

1-Methoxycarbonyl-2-methyl-2,6-dihydronaphth[1,2,3-c,d]indole-6-thione (IIIb). A 0.2-g quantity (0.7 mmole) of methyl N-methylpyrroloanthronecarboxylate (IIb) was dissolved in 15 ml of dioxane, 0.2 g (1 mmole) of phosphorus pentasulfide was added, and the mixture was refluxed for 15 min, after which it was filtered while still hot. To the hot filtrate, 15 ml of hot water was added. The precipitate was filtered off and washed with water.

2-Methyl-6-methylthionaphth[1,2,3-c,d]indolium Methylsulfate (IVa). A 0.7 g quantity (2.8 mmoles) of the thione IIIa in 3 ml of neutral dimethyl sulfate was heated for 30 min at 100°C. The product separated out in the course of heating. After cooling, ether was added to the reaction mixture, and the precipitate was filtered off and washed with ether.

2-Methyl-6-dicyanomethylene-2,6-dihydronaphth[1,2,3-c,d]indole (V). A mixture of 0.38 g (1 mmole) of the salt IVa and 0.15 g (2.2 mmoles) of malonodinitrile in 5 ml of acetonitrile with 10 drops of triethylamine was refluxed for 10 min. The precipitate that formed upon cooling was filtered off and washed with ether.

2-[2-Methyl-2,6-dihydronaphth[1,2,3-c,d]indol-6-ylidene]methyl-3-ethylbenzothiazolium Perchlorate (VI). A mixture of 0.13 g (0.57 mmole) of 2-methyl-3-ethylbenzothiazolium perchlorate and 0.19 g (0.5 mmole) of the salt IVa in 5 ml of acetonitrile with 2 drops of triethylamine was refluxed for 20 min. The intensely blue solution was evaporated to dryness. The residue was milled with water, filtered off, and then washed with water and ether.

2,6-Diphenyl-4-[2-methyl-2,6-dihydronaphth[1,2,3-c,d]indol-6-ylidene]methylpyrylium Perchlorate (VIIa). A 0.173-g quantity (0.5 mmole) of 2,6-diphenyl-4-methylpyrylium perchlorate was dissolved in 10 ml of acetonitrile, 0.19 g (0.5 mmole) of the salt IVa, and 0.04 g of anhydrous sodium acetate were added, and the mixture was refluxed for 20 min. After cooling, the reaction mixture was diluted with water. The precipitate was filtered off and washed with water and ether.

2,6-Diphenyl-4-[2-methyl-2,6-dihydronaphth[1,2,3-c,d]indole-6-ylidene]methylthiopyrylium Perchlorate (VIII). A mixture of 0.19 g (0.5 mmole) of 2,6-diphenyl-4-methylthiopyrylium perchlorate, 0.19 g of the salt IVa, and 0.04 g of anhydrous sodium acetate in 5 ml of acetonitrile was refluxed for 10 min. The precipitate that formed upon cooling was filtered off and washed with water and ether.

2,6-Diphenyl-4-[1-methoxycarbonyl-2-methyl-2,6-dihydronaphth[1,2,3-c,d]indol-6-ylidene]methylpyrylium Perchlorate (VIIb). A 0.2 g quantity (0.65 mmole) of the thione IIIb in 0.5 ml of neutral dimethyl sulfate was heated for 10 min at 100°C. After cooling, the mixture was milled with dry ether. The residue, a viscous mass with λ_{max} 500 nm, was used without purification or analysis in the synthesis of the dye. A mixture of 0.173 g (0.5 mmole) of 2,6-diphenyl-4-methylpyrylium perchlorate and the methylthio derivative IVb was dissolved in 5 ml of acetonitrile, 0.04 g of anhydrous sodium acetate was added, and the mixture was refluxed for 10 min. After cooling, the dye was precipitated by adding water. The precipitate was filtered out and washed with water and ether.

LITERATURE CITED

1. A. I. Tolmachev, Yu. L. Slominskii, and M. A. Kudinova, *Usp. Nauchn. Fotogr.*, **22**, 12 (1984).
2. G. G. Dyadyusha and A. D. Kachkovskii, *Ukr. Khim. Zh.*, **44**, 948 (1978).
3. F. A. Mikhailenko, N. P. Vasilenko, A. D. Kachkovskii, and Yu. I. Rozhinskii, *Zh. Org. Khim.*, **18**, 435 (1982).
4. G. G. Dyadyusha and A. D. Kachkovskii, *Teor. Éksp. Khim.*, **15**, 152 (1979).
5. G. G. Dyadyusha, A. D. Kachkovskii, and M. L. Dekhtyar', *Ukr. Khim. Zh.*, **54**, 406 (1988).
6. M. V. Kazankov, N. P. Makshanova, and E. G. Kuznetsova, *Khim. Geterotsikl. Soedin.*, No. 8, 1103 (1977).
7. M. V. Kazankov and E. G. Sadovykh, *Khim. Geterotsikl. Soedin.*, No. 10, 1356 (1978).
8. C. E. Mees and T. H. James, *Theory of the Photographic Process*, 3rd edn., Macmillan, New York (1966).
9. A. I. Kiprianov, *Color and Structures of Cyanine Dyes* [in Russian], Naukova Dumka, Kiev (1979).
10. A. J. Gordon and R. A. Ford, *The Chemist's Companion*, Wiley, New York (1972).