Structures of terminal heterocyclic groups and fluorescence-spectral properties of polymethine dyes

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The fluorescence and absorption bands of carbocyanines containing pyrylium or benzoxazolium groups, their nitrogen-, sulfur-, and selenium-containing analogs, their benzohomologs, or isomeric analogs of pyrylium as terminal groups were mathematically processed using the method of moments. The regularities in the displacement of the absorption and fluorescence bands following the replacement of the heteroatom and variations of the positions of substituents in the terminal groups were explained using perturbation theory. Based on quantum-chemical calculations, the changes in the bond orders in the ground and excited states of the dyes were studied. The correlations between the moments of the experimental absorption and fluorescence bands and the frequency and the form of the chromophore vibrations were analyzed. The transition from pyrylo-4-cyanines to isomeric pyrylo-2-cyanines leads to substantial broadening of the bands, an increase in the Stokes shifts, decreases in the coefficients of asymmetry, kurtosis, and fine structure of the bands, as well as a decrease in the quantum yield of fluorescence.

Key words: polymethine dyes, heterocyclic groups; vibronic interactions; fluorescence-spectral properties.

The relationship between the fluorescence-spectral properties of polymethine (cyanine) dyes (PD) and the structures of their terminal heterocyclic groups (heterocyclic residues) is of interest in the target-directed search for heterocyclic compounds that can be used for the synthesis of promising PD.[1] Owing to the development of computer chemistry,[2] it has become possible to carry out the computer selection of the desired heterocyclic molecules.

It is convenient to use trimethinecyanines (carbocyanines) as examples to study the relationship between the fluorescence-spectral properties of PD and the structure of heterocyclic residues. The molecules of carbocyanines, unlike those of monomethinecyanines, experience no effects due to close arrangement of the heterocyclic nuclei.[3] At the same time, carbocyanines are solvated much more weakly[4] than dyes containing longer polymethine chains.

The purpose of the present study is to elucidate the relationship between the structure of heterocyclic residues and the fluorescence-spectral properties of polymethine dyes in various trimethinecyanines.

Experimental

Absorption and fluorescence spectra of the dyes were measured on SF-20 and SDL-1 spectrophotometers. Argon, helium-neon, and krypton lasers were used as fluorescence excitation sources. To increase the sensitivity of the signal recording, an FEU-83 photoelectron multiplier cooled to −40 °C was used.

To estimate quantitatively the variations in the electronic spectra of cyanines, their long-wavelength absorption and fluorescence bands were processed in terms of the method of moments.[5] This allowed us to obtain additional data concerning the bands, namely, the mean positions (M_a^{-1}, M_f^{-1}), oscillator strength (f), band widths (σ^a, σ^f), asymmetry coefficients ($\gamma_1{}^a$, $\gamma_1{}^f$), kurtoses ($\gamma_2{}^a$, $\gamma_2{}^f$), and the fine structures (F^a, F^f),[6] in addition to the usual fluorescence-spectral characteristics, *viz.*, the maxima of the bands ($\lambda^a{}_{max}$, $\lambda^f{}_{max}$) and their molar extinction coefficients (ε), and the quantum yields of fluorescence (φ) (indices "a" and "f" refer to absorption and fluorescence spectra, respectively).

The moments in the absorption spectra were found in ε/ν—ν coordinates, and those in the fluorescence spectra were determined in W/ν^4—ν coordinates (ν is the wave number, and W is the fluorescence intensity), which permitted the most legitimate comparison of the moments of the absorption and fluorescence bands.[5] The Stokes shifts were found from the maxima (SS_λ) and the mean (SS_m) positions of the bands, respectively. The φ values were measured by a relative method.[7]

The quantum-chemical calculations of the squared variations (δ) of bond orders (P) upon excitation were carried out by the Hückel molecular orbital (MO) method using a set of parameters for atoms and bonds taken from the literature.[8] The δ value is normally used to describe vibronic interactions (VI) in the molecules of PD (see Ref. 5).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 2194—2203, September, 1996.

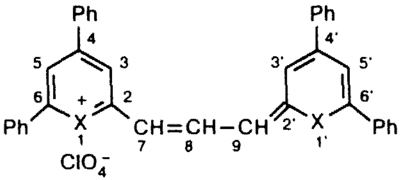
Table 1. Characteristics of long-wavelength absorption bands of PD **1—13** (in CH_2Cl_2) and δ values

PD	λ^a_{max} /nm	$\varepsilon \cdot 10^{-4}$ /L mol^{-1} cm^{-1}	M_a^{-1} /nm	f	σ^a /cm^{-1}	γ_1^a	γ_2^a	F^a	δ
1	800	8.51	739.6	0.78	1176	1.17	2.2	0.064	0.1762
4	686	25.1	665.1	1.21	801	1.57	3.3	0.105	0.1158
2	865	7.08	820.2	0.79	1058	1.07	1.8	0.046	0.1630
5	762	24.5	743.2	1.16	729	1.53	3.2	0.100	0.1133
3	630	9.33	604.6	0.88	1060	1.00	2.0	0.041	0.1656
6	644	18.6	627.9	1.20	870	1.80	5.4	0.096	0.1196
7	805	25.3	783.9	1.12	669	1.47	3.0	0.098	0.1110
8	740	9.77	697.2	0.97	1056	1.03	1.5	0.045	0.1543
9	820	9.12	779.9	0.91	917	0.97	1.4	0.036	0.1460
10	635	13.5	617.5	1.02	942	1.31	3.2	0.055	0.1562
11	706	10.5	674.7	0.78	964	1.49	3.2	0.108	0.1426
12	713	10.7	670.0	0.86	1084	1.25	2.5	0.071	0.1884
13	715	20.4	695.9	0.83	772	1.60	3.4	0.110	0.1131

Results and Discussion

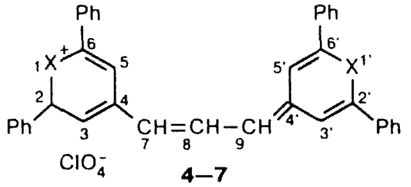
The molecular design of the terminal heterocyclic groups in the dyes under study was based on different variations of the structure of heterocyclic residues. The effects of isomerism in the heterocyclic residues, of the annelation of their bonds, and of the electronic and steric influences of substituents occupying various positions in the terminal groups on the positions, intensities, and shapes of the long-wavelength absorption and fluorescence bands of carbocyanines were studied.

Isomerism in the heterocyclic residues. The effect of the isomerism in the heterocyclic residues on the fluorescence-spectral properties of PD was considered for pyrylocyanines and their heteroanalogs of the α- (2-substituted isomers **1—3**) and γ-series (4-substituted isomers **4—7**) described previously.[9]



1—3

X = O (**1**), S (**2**), NMe (**3**)



4—7

X = O (**4**), S (**5**), NMe (**6**), Se (**7**)

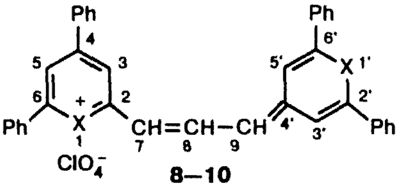
The characteristics of the long-wavelength absorption and fluorescence bands of these compounds are listed in Tables 1 and 2, respectively. It can be seen that pyrylo-2- and thiopyrylo-2-cyanines (PD **1** and **2**) absorb and fluoresce at markedly longer wavelengths than the corresponding 4-isomers (PD **4** and **5**). For example, λ^a_{max} and λ^f_{max} of the former are shifted by 100—110 nm with respect to these values of the latter, and M_a^{-1} and M_f^{-1} are displaced by 65—75 nm. However, in the case of isomeric pyridocyanines **3** and **6**, the opposite situation is observed (see Tables 1 and 2). This is due to the fact that the C—C bonds in the heterocyclic residues of pyrylo-2- and thiopyrylo-2-cyanines participate in the common system of conjugation to a lesser degree than those in pyrido-2-cyanines, because O and S atoms are less likely to be involved in conjugation than N atoms.[9] Therefore, in the molecules of PD **1** and **2**, the X(1)C(6)C(5)C(4)C(3)C(2)C(7)C(8)C(9)C(2')—C(3')C(4')C(5')C(6')X(1') chain of atoms acts as the main chromophore, while in the case of PD **3**, the main chromophore is X(1)C(2)C(7)C(8)C(9)C(2')X(1'). Since the former is longer, pyrylo-2- and thiopyrylo-2-cyanines are more intensely colored and exhibit luminescence at longer wavelengths than their nitrogen-con-

Table 2. Characteristics of the long-wavelength fluorescence bands of PD **1—13** (in CH_2Cl_2)

PD	λ^f_{max} /nm	φ (%)	M_f^{-1} /nm	σ^f /cm^{-1}	$-\gamma_1^f$	γ_2^f	F^f	SS_λ	SS_m
								cm^{-1}	
1	840	1.0	869.0	1070	1.12	1.9	0.058	595	2013
4	702	9.0	729.8	760	1.49	2.8	0.102	332	1332
2	933	0.2	986.3	880	1.16	2.1	0.061	843	2053
5	813	2.0	854.1	634	1.58	3.3	0.113	822	1747
3	660	1.5	676.2	910	1.15	2.0	0.060	722	1751
6	673	7.0	697.0	805	1.44	2.5	0.087	669	1579
7	866	0.05	913.0	551	1.42	2.3	0.096	875	1804
8	760	4.0	789.2	865	1.19	2.2	0.070	356	1672
9	875	0.8	918.5	770	1.23	2.6	0.075	777	1935
10	663	3.0	686.0	850	1.29	2.3	0.064	665	1617
11	724	4.5	754.3	910	1.46	3.0	0.105	352	1564
12	738	2.0	772.4	1002	1.21	2.2	0.067	475	1979
13	732	9.5	765.2	730	1.53	3.0	0.106	325	1301

taining analogs or 4-isomers. On the other hand, the chromophore in the molecules of pyrido-2-cyanines is shorter than in the case of pyrido-4-cyanines (in the latter compounds, it includes the whole chain of conjugation X(1)C(2)[C(6)]C(3)[C(5)]C(4)C(7)C(8)C(9)—C(4′)C(5′)[C(3′)]C(6′)[C(2′)]X(1′)). Therefore, the bands in the electronic spectra of the former are shifted hypsochromically with respect to those of the latter.

The validity of the above explanation is supported by the fluorescence-spectral properties of cyanines **8—10** (see Tables 1 and 2).[10] The bands in the electronic spectra of compounds **8** and **9** are shifted bathochromically with respect to the similar bands for PD **4** and **5** and shifted hypsochromically compared to those for cyanines **1** and **2**. Conversely, (pyrido-2)(pyrido-4)carbocyanine **10** absorbs and emits at shorter wavelengths than its 4-substituted isomer **6** but at longer wavelengths than its 2-isomer **3** (see Tables 1 and 2). Such an arrangement of the absorption and fluorescence bands of PD **8—10** with respect to those for their heteroanalogs of the α- and γ-series is possible only if the main chromophore in compounds **8** and **9** includes the X(1)C(6)C(5)C(4)C(3)C(2)C(7)C(8)C(9)C(4′)—C(5′)[C(3′)]C(6′)[C(2′)]X(1′) chain of atoms, while that in cyanine **10** includes the X(1)C(2)C(7)C(8)C(9)—C(4′)C(5′)[C(3′)]C(6′)[C(2′)]X(1′) moiety.



8—10

X = O (**8**), S (**9**), NMe (**10**)

At first glance, the shapes of the bands in the electronic spectra of isomeric PD **1—3** and **4—6** should not differ substantially from one another, because their chromophore chains are confined between two identical heteroatoms. Unexpectedly we found that the numerical values for the squared variations of the bond orders in pyrylo-2-cyanine and its heterocyclic analogs are markedly greater than the corresponding values for the 4-isomers (see Table 1). In fact, on going from the 4-isomers to the 2-isomers, substantial broadening of the bands in the electronic spectra and a decrease in their asymmetry, kurtosis, and degree of structurization have been observed experimentally. The enhancement of VI that occurs in this case is in good agreement with the increase in the Stokes shifts (see Tables 1 and 2).

Analysis of the changes in the orders of individual bonds after excitation indicates that the enhancement of the electron vibrational interactions in the 2-isomers is caused by the dramatic decrease in the C(3)—C(4) bond order during excitation (Table 3). This decrease is much more pronounced than the changes in the orders of any other bond, and therefore it contributes substantially (by ~1/3) to the value of δ.

The dominant role of the C(3)—C(4) bond in the variation of the shapes of the bands in the case of the 2-isomers is confirmed by comparing the absorption and fluorescence spectra of symmetrical PD **1—6** with the corresponding spectra of asymmetrical cyanines **8—10**, which are based on the same heterocyclic systems as the symmetrical dyes of the α- and γ-series isomeric to them. The bands in the electronic spectra of cyanines **8—10** are broader than those for the related PD **4—6**, but are narrower than the bands exhibited by PD **1—3** (see Tables 1 and 2). This difference in the σ^a and σ^f values is in good agreement with the calculations of δ; for the asymmetrical cyanines **8—10**, the values of δ are greater than those for the 2-isomers but smaller than those for the 4-isomers.

The symmetrical pyrylo-2-cyanines and their heteroanalogs incorporate two bonds (one in each nucleus), whose vibrations cause substantial broadening of the bands. The replacement of one of the nuclei by an isomeric nucleus, *i.e.*, by the C(4) atom attached to the chromophore, leads to the disappearance of one of these bonds; consequently, the fluorescence and absorption bands of the asymmetrical PD **8—10** are narrower than the bands corresponding to the symmetrical cyanines **1—3**. However, if compounds **8—10** possessed substantial electron asymmetry, this could compete with the effect of the C(3)—C(4) bond, and in this case, their bands would be broader than those of both related dyes. Apparently, the presence of electron asymmetry in compounds **8—10** exerts a greater effect on the higher moments of the bands, because the γ_1^a, γ_2^a, F^a and γ_1^f, γ_2^f, F^f values for PD **8** and **9** are lower than those found for the related PD **1**, **2** and **4**, **5** (see Tables 1 and 2). The presence of even one C(3)—C(4) bond, whose order

Table 3. Orders of the π-bonds in PD **1** and **4** in the ground (P^0) and excited (P^*) states

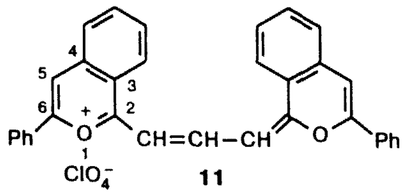
PD	P^0 (P^*)							
	O—C(2)	C(2)—C(3)	C(3)—C(4)	C(4)—C(5)	C(5)—C(6)	O—C(6)	C(2)—C(7), C(4)—C(7)	C(7)—C(8)
1	0.3799 (0.3318)	0.5774 0.6303	0.6698 (0.5968)	0.5629 (0.5750)	0.7138 (0.6878)	0.4062 (0.3753)	0.5820 (0.5491)	0.6516 (0.6358)
4	0.4026 (0.3677)	0.7303 (0.7129)	0.5285 (0.5304)	0.5285 (0.5304)	0.7303 (0.7129)	0.4026 (0.3677)	0.5581 (0.5171)	0.6560 (0.6369)

substantially decreases after excitation, in the cations derived from the asymmetrical cyanines **8**—**10** leads to broadening of their bands in the electronic spectra with respect to those of the symmetrical pyrylo-4-cyanines and their heteoanalogs.

In the ground and excited states of the heterocyclic residues of the 2-isomers, strong alternation of bond orders occurs. This is somewhat less pronounced in the S_1 state (see Table 3); therefore, the numerical values of σ^f, γ_1^f, γ_2^f, and F^f for the 2-isomers are smaller than the values of σ^a, γ_1^a, γ_2^a, and F^a (see Tables 1 and 2). In the ground state, the C(3)—C(4) and C(5)—C(6) bonds are close to double bonds, while the rest of the bonds in the heterocyclic residues are close to single bonds (see Table 3). This conclusion, which follows from quantum-chemical calculations, is confirmed by the data[11] of an X-ray structural study of PD **2**. Of the bonds in the molecules of the 2-isomers, the C(3)—C(4) bond is the shortest; therefore, its order can decrease (or its length can increase) the most upon excitation.

The isomerism in the heterocyclic residues also has a substantial effect on the intensities of the bands in the electronic spectra of PD. Pyrylo-2-cyanines and their heteroanalogs have considerably smaller ε, f, and φ values than the corresponding PD of the γ-series (see Tables 1 and 2). The decrease in the extinction coefficients and in the oscillator strengths on going from the 4-isomers to the 2-isomers results from the broadening of the absorption bands. Since, as noted above, this broadening is due to the enhancement of the VI, the decrease in the ε and f parameters on going from the 2-isomers to the 4-isomers is due to the increase in these interactions. The enhancement of the VI should also decrease the quantum yield of fluorescence of PD **1**—**3** with respect to that for PD **4**—**6**; however, the decrease in φ can be also due to enhancement of the internal conversion. This suggestion is based on the fact that pyrylo-2- and thiopyrylo-2-cyanines are substantially more intensely colored than their 4-isomers ($\Delta\lambda \approx$ 100—110 nm). Therefore, according to the published data,[12] one may expect that the internal conversion would be enhanced and, hence, the φ value would decrease upon passing from PD **1** and **2** to their isomers **4** and **5**, due to the decrease in the energy gap between the S_0 and S_1 states over this series of dyes. However, the variation of the quantum yield of fluorescence of the isomeric pyridocyanines **3** and **6** follows the same trend, despite the fact that PD **3** absorbs at shorter wavelengths than PD **6** (see Tables 1 and 2). Thus, the decrease in φ on going from the 4-isomer to the 2-isomers is mostly due to the enhancement of the VI.

Annelation of the heterocyclic residues. Any variation in the structures of the heterocyclic nuclei of the 2-isomers that hampers elongation of the C(3)—C(4) bond, should lead to narrowing of the fluorescence and absorption bands and to an increase in their asymmetry, kurtosis, and degree of structurization. Therefore, one may expect that the annelation of pyrylo-2-carbocyanine **1** at this bond would lead to the above-mentioned changes in the shape of the bands. The fact is that the C(3)—C(4) bond in the ground state of PD **1** is closer to a double bond (P^0 = 0.6698), whereas in the excited state, it is closer to a single bond (P^* = 0.5968), *i.e.*, its order varies. Annelation at this bond should make it a one-and-one-half bond, and, hence, should decrease substantially the range of elongation of the C(3)—C(4) bond after excitation. In fact, this bond in isobenzocarbocyanine **11** makes a contribution of only 4% to the overall δ value, whereas in the case of the non-annelated PD **1**, it accounts for 34% of all the VI in the molecule. Consequently, as was suggested, the bands in the electronic spectra of isobenzocarbocyanine **11** become substantially narrower, and their asymmetry coefficients, kurtoses, and fine structures become greater than those in the spectra of pyrylo-2-carbocyanine **1** (see Tables 1 and 2).



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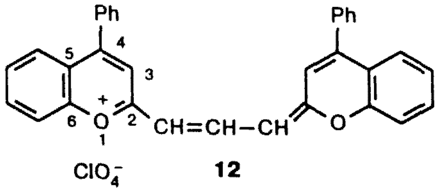

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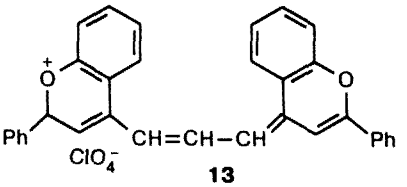


13

The annelation of other bonds may cause opposite effects. For example, the introduction of a benzene ring at the C(5)—C(6) bond of the molecule of PD **1** (compound **12**)[13] brings the C(4)—C(5) bond even closer to a single bond. This fact should be favorable for an increase in the order of the C(3)—C(4) bond in the ground state, and, hence, should increase the range in which it varies upon excitation. In fact, in the case of benzocarbocyanine **12**, this bond is responsible for 40% of the VI in the whole molecule; therefore the fluorescence and absorption bands exhibited by PD **12** are substantially broader, more symmetrical, and more diffuse than the corresponding bands in the spectra of isomers **11** and **13** (see Tables 1 and 2).

Nature of the heteroatom. Pyrylocyanines and their analogs are fairly convenient and simple objects for which to investigate the effect of the nature of the heteroatom on the fluorescence-spectral properties of PD. These molecules contain only one heteroatom in a key position of the chromophore, and this atom strongly affects the main electron transition.

According to MO perturbation theory,[14] the change in the transition energy ($\delta\Delta E$) following substitution of the heterocyclic residues is described by the equation

$$\delta\Delta E = \Delta q_X \delta\alpha_X + 2\ \Sigma\Delta P_{CX}\delta\beta_{CX}, \qquad (1)$$

where Δq_X and ΔP_{CX} are the changes in the electron density on the atoms and in the orders of the C—X bonds upon excitation, respectively; and $\delta\alpha_X$ and $\delta\beta_{CX}$ are the changes in the Coulomb and resonance integrals after the replacement of the X atom. It should be borne in mind that the ΔE, Δq, and ΔP values in Eq. (1) are the differences between the corresponding values for the excited and ground states, and α_X and β_{CX} are smaller than 0.

The electron density on the O atoms of pyrylocyanines increases during excitation ($\Delta q > 0$), while the C—O bond orders decrease ($\Delta P < 0$). For example, for PD **1**, $\Delta q_O = 0.0256$, $\Delta P_{C(2)O} = -0.0481$, and $\Delta P_{C(6)O} = -0.0310$. When the O atoms are replaced by S or Se atoms, the $\delta\alpha_X$ and $\delta\beta_{CX}$ are greater than 0. Thus, the first term of Eq. (1) becomes positive, while the second term is negative. Since the changes in the C(2)—O and C(6)—O bond orders are more significant than the change in the electron density on the O atom after excitation, the second term in Eq. (1) should be greater in magnitude than the first term, especially as it is doubled; consequently, $\delta\Delta E$ becomes less than zero. This means that the replacement of heteroatoms considered above should result in a decrease in the energy of the transition, and, hence, in a bathochromic shift of the bands. For example, according to Eq. (1), on passing from PD **1** to **2**, it amounts to 66 nm (954 cm^{-1}) at $\beta = -31200$ cm^{-1}, which is in agreement with experimental results (see Tables 1 and 2). However, it is noteworthy that the bathochromic shifts of bands in the fluorescence spectra are greater than those in the absorption spectra. For example, upon transition from PD **1** to PD **2**, the bathochromic shift of λ^f_{max} is 93 nm (1487 cm^{-1}) and that of λ^a_{max} is only 65 nm (939 cm^{-1}). A similar substitution in the 4-isomers leads to more substantial changes, and the bathochromic shifts of λ^f_{max} and λ^a_{max} are equal to 111 and 76 nm (1945 and 1454 cm^{-1}), respectively. The transition from thiopyrylo-4-cyanine **5** to selenopyrylo-4-cyanine **7** is also accompanied by bathochromic shifts of the fluorescence and absorption bands. However, the difference between the λ^f_{max} and λ^a_{max} values is much smaller; they are equal to 53 and 43 nm (753 and 701 cm^{-1}), respectively. The fact that the bathochromic shifts of the fluorescence bands following the replacement of the O atoms in pyrylocyanines by S and Se atoms are greater than the shifts of the absorption bands accounts for the increase in the Stokes shifts in the series O, S, Se (see Table 2).

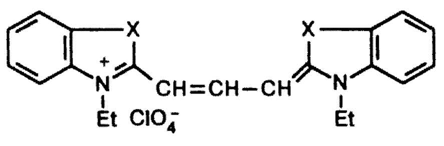
The foregoing regularities are followed not only by the maxima but also by the mean positions of the bands in the fluorescence and absorption spectra (see Tables 1 and 2).

In conformity with Eq. (1), it should be expected that the transition from pyrylocyanines **1** and **4** to the corresponding pyridocyanines **3** and **6** (similarly to the transition to thiopyrylocyanines **2** and **5**) would be accompanied by a bathochromic shift of bands, since $\alpha_N < \alpha_O$ and $|\beta_{CN}| < |\beta_{CO}|$.[8] However, the opposite effect was observed experimentally. When the O atoms in pyrylocyanines are replaced by NMe groups, a hypsochromic shift of λ^f_{max}, λ^a_{max}, M_f^{-1}, and M_a^{-1} occurs (see Tables 1 and 2). In the fluorescence spectra, these shifts are smaller than in the absorption spectra. For example, when the O atoms in pyrylo-2- and pyrylo-4-cyanines are replaced by NMe groups, $\Delta\lambda^f_{max} = 180$ and 29 nm (3247 and 614 cm^{-1}), while $\lambda^a_{max} = 170$ and 42 nm (3373 and 951 cm^{-1}), respectively. However, as in the case of thiopyrylocyanines, the Stokes shifts for pyridocyanines are greater than those for pyrylocyanines. This increase in SS_λ is due to the fact that the hypsochromic shifts of the fluorescence bands following the replacement of the O atoms in pyrylocyanines by NMe groups are smaller than the shifts of the absorption bands.

Due to steric effects of the heteroatom, the phenyl groups in the ground states of molecules **1—7** deviate from the plane of the chromophore through different angles. These angles amount to 0—10° in the molecules of pyrylocyanines, ~40° in the molecules of thio- and selenopyrylocyanines, and 60° in the case of pyridocyanines (see Ref. 15). It follows from the results of quantum-chemical calculations[16] that the carbon—heteroatom bonds are substantially elongated in the excited state. This diminishes the steric restrictions to the rotation of the phenyl groups; therefore, after excitation, the Ph groups are able to enter the plane of the chromophore to a substantial extent. This arrangement of the Ph groups is also facilitated by the fact that in the S_1 state, the orders of the C—Ph bonds increase.[16] The fact that the torsion angles between the planes of the Ph groups and the chromophore plane in the excited state of PD are smaller than in the ground state results in larger bathochromic shifts in the fluorescence spectra than in the absorption spectra. These effects are more pronounced in the case of thiopyrylo-, selenopyrylo-, and pyridocyanines than for pyrylocyanines, since the angles of rotation of the Ph groups in the former compounds are greater than those in the latter compounds.[15] The groups mentioned above have a greater effect on the positions of bands in the spectra of 4-isomers than on those of 2-isomers, since in the former case, all the Ph groups emerge from the chromophore plane in the ground state, while in the latter case, only the two groups that are located close to the heteroatom deviate from the plane.

Due to the different angles of rotation of the Ph groups in compounds **1—7**, *i.e.*, the different degrees of their participation in conjugation, the position of the fluorescence and absorption bands after replacement of the heteroatoms is determined not only by their electronic effects, which are described by Eq. (1), but also by steric effects. Among the dyes studied, the latter are maximum in the case of pyridocyanines. Conversely, according to Eq. (1), when the O atoms in pyrylocyanines are replaced by NMe groups, the electronic effects become weaker than in the case of S and Se atoms, since $\alpha_N > \alpha_S(\alpha_{Se})$, and $|\beta_{CN}| > |\beta_{CS}|(|\beta_{CSe}|)$.[8] Thus, the variation of the λ^a_{max}, λ^f_{max}, M_a^{-1}, and M_f^{-1} parameters on going from pyrylocyanines to pyridocyanines is largely governed by the steric effects of the heteroatoms rather than by their electronic effects, which are crucial in the case of the transition to thiopyrylocyanines and selenopyrylocyanines. Therefore, when the O atoms in pyrylocyanines are replaced by NMe groups, the fluorescence and absorption bands undergo a hypsochromic shift (see Tables 1 and 2) rather than a bathochromic shift, which should have been expected from perturbation theory (see Eq. (1)). The validity of the foregoing is confirmed by the fact that a similar replacement in the molecules of analogs of PD **1**, **3**, and **6**, which contain Me groups in place of the Ph groups, results in an enhancement of the color, in conformity with Eq. (1).[17]

A similar effect occurs on going from PD **14**, which belongs to another structural type, to PD **15** (Table 4).



14—17

X = NEt (**14**), O (**15**), S (**16**), Se (**17**)

The replacement of the O atoms by S and Se atoms in the series of PD **15—17**, similarly to that in the series of cyanines **4**, **5**, and **7**, causes bathochromic shifts of λ^a_{max} and λ^f_{max}. However, the magnitudes of these effects are smaller (see Tables 1, 2, and 4), since the heteroatoms that are replaced in PD **15—17**, unlike those in compounds **4**, **5**, and **7**, are located in nonterminal positions of the chromophore.

Table 4. Characteristics of the long-wavelength fluorescence and absorption bands of PD **14—17** (in CH_2Cl_2)

PD	λ^a_{max} /nm	σ^a /cm^{-1}	λ^f_{max} /nm	σ^f /cm^{-1}	SS_λ /cm^{-1}	δ
14	494	985	512	979	712	0.1853
15	490	967	507	963	684	0.1738
16	560	892	580	887	616	0.1807
17	576	876	597	870	611	0.1823

Since the steric effect of the NMe group on the phenyl groups is more pronounced than that of the S and Se atoms, these groups enter the plane of the chromophore in the excited states of pyridocyanines to a lesser degree than in the thiopyrylocyanines or selenopyrylocyanines. Therefore, the Stokes shifts for the former are lower than those for the latter. It is significant that when a similar substitution of the heteroatoms occurs in the series of PD **15**, **16**, and **17**, which contain no groups capable of decreasing the torsion angle with the chromophore plane, the SS_λ values vary in the opposite order (see Tables 2 and 4).

The changes in the widths of the fluorescence and absorption bands on going from pyrylocyanines to thiopyrylocyanines and selenopyrylocyanines are in good agreement with the results of the calculation of the δ values (see Tables 1 and 2). It should be noted that the variation of the bond orders in the Ph groups of dyes **1—7** upon excitation is substantially smaller than that in the main chromophore, and, consequently, the VI in these compounds are relatively insensitive to the angles of rotation of the Ph groups and are mostly determined by the nature of the heteroatom. Therefore unlike the Stokes shifts, the variation of the widths of the fluorescence and absorption bands of the dyes under consideration as a function of the nature of atom X is in good agreement with the calculated δ value (see Tables 1 and 2). However, the fact that the values of σ^a, σ^f, and δ vary in parallel on going from pyrylocyanines to thiopyrylocyanines and selenopyrylocyanines does not indicate by itself that the widths of the bands are determined by the VI. The fact is that the narrowing of bands in the electronic spectra in the above series of PD may be caused not only by weakening of the VI but also by increases in the atomic weight of the heteroatom, which should result in a decrease in the frequency of the fully symmetrical vibration ν_k of the chromophore atoms:[16]

$$\sigma = \delta\sqrt{\mathrm{const}\ K\nu_k}\,, \tag{2}$$

$$\gamma_1 = \nu_k/\delta\sqrt{\mathrm{const}\ K}\,, \tag{3}$$

$$\gamma_2 = \nu_k/\sigma^2\mathrm{const}K - 3. \tag{4}$$

Here, the characteristics of the shapes of the bands in the experimentally obtained electronic spectra of cyanines are related to the parameters of their molecules, *viz.*, δ, ν_k, and K (the force constant). The increase in the atomic weight is matched by a decrease in the $\gamma_1{}^a$, $\gamma_2{}^a$, and F^a values (see Eqs. (2)—(4)) following the transition from pyrylocyanines to thiopyrylocyanines and selenopyrylocyanines (see Table 1). However, these changes in the asymmetry coefficients, kurtoses, and fine structures can also be due to the enhancement of the nucleophilic solvation that occurs when the pyrylium groups are replaced by the less electron-donating thiopyrylium and selenopyrylium residues.[4] Based only on analysis of the absorption spectra, one cannot unambiguously answer the question of whether the "heavy" atom effect or solvation is the crucial factor that determines the changes of the σ^a, $\gamma_1{}^a$, $\gamma_2{}^a$, and F^a values on going from PD **1** to **2** and from PD **4** to **5** and **7**. To answer this question, it is necessary to consider also the fluorescence spectra, since the shapes of fluorescence bands are relatively insensitive to changes in the nature of the solvent[18] and are mostly determined by the VI. It can be seen from Table 2 that the increase in σ^f after the replacement of the O atoms in pyrylocyanines by S atoms is accompanied by an increase in $\gamma_1{}^f$, $\gamma_2{}^f$, and F^f, which differs from the behavior of the corresponding parameters in the absorption spectra. This unambiguously indicates that the narrowing of the fluorescence and absorption bands that accompanies the transitions from PD **1** to **2** and from PD **4** to **5** is mostly due to the weakening of the VI (see Eqs. (2)—(4)). The replacement of the O or S atoms by Se atoms causes a decrease in $\gamma_1{}^f$, $\gamma_2{}^f$, and F^f (see Table 2). This indicates that the "heavy" atom has a crucial effect on the variation of the shapes of the bands.

It is significant that a similar substitution of the heteroatom in the series of carbocyanines **15—17** also results in narrowing of the fluorescence and absorption bands. However, in these compounds, unlike PD **1**, **2** and **4**, **5**, **7**, the narrowing is accompanied by an increase in δ (see Table 4). Thus, in the case of carbocyanines **15—17**, in which the heteroatoms do not occupy the terminal position in the chromophore, the presence of a "heavy" atom exerts a crucial effect on the band widths in the electronic spectra (see Eq. (2)).

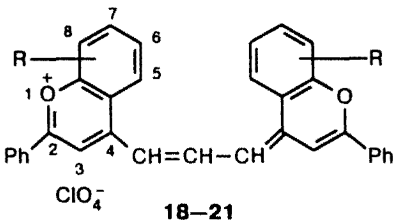
The transition from pyrylocyanines to thiopyrylocyanines and selenopyrylocyanines is accompanied by quenching of the fluorescence (see Table 2). Apparently, this is due to enhancement of the internal conversion, since the above-mentioned transition leads to a substantial decrease in the energy gap between the S_0 and S_1 states. The intercombination conversion, whose probability should increase after the introduction of heavy atoms into the dye molecule, may make an additional contribution to the decrease in the value of φ.[5]

The changes in the parameters σ^a and σ^f after the replacement of the O atoms in pyrylocyanines **1** and **4** and in oxacarbocyanine **15** by NMe (or NEt) groups is in good agreement with the calculated δ values (see Tables 1, 2, and 4). In this case, based only on the absorption spectra, one can state with confidence that the widths of the bands are determined by the VI, since the frequencies of the stretching vibrations of the C—O, C—N, and C—C bonds are quite close, and, therefore, the ν_k values for the PD incorporating oxygen- and nitrogen-containing heterocyclic residues should be virtually identical.

For both types of isomers, the narrowing of the absorption bands after the replacement of the O atoms by the NMe group does not lead to an increase in the $\gamma_1{}^a$, $\gamma_2{}^a$, and F^a parameters, but, conversely, results in their decrease. This is not inconsistent with the trend in the variation of the VI in the pyridocyanines and pyrylocyanines, since the former undergo more extensive nucleophilic solvation,[4] due to the more pronounced electron-donating properties of their heterocyclic residues.[5] It is this solvation that violates the trend in the variation of the asymmetry coefficients, kurtoses, and fine structures typical of uniformly broadened bands (see Eqs. (2)—(4)). In the fluorescence spectra, in which the effect of the nucleophilicity of the solvent on the shapes of bands is insignificant, the decrease in σ^f on going from PD **1** to **3** and from PD **6** to **4** is accompanied by an increase in the coefficients $\gamma_1{}^f$, $\gamma_2{}^f$, and F^f, as should be expected for vibronic bands with the Poisson distribution of intensities (see Eqs. (2)—(4)).

Nature of the substituent. Let us consider first the effect of the substituent on the fluorescence-spectral properties of PD as a function of its position in the heterocyclic residue. For this purpose, it is better to use PD with electron-donating substituents, since, according to the sensitivity rule,[19] heterocyclic residues with weak electron-donating properties in the cyanine molecules should exert greater effects on the spectra than electron-withdrawing groups.

Tables 5 and 6 present the characteristics of long-wavelength fluorescence and absorption bands of methoxy-substituted flavylocarbocyanines **18—21**.[20]



18—21

R = 5-OMe (**18**), 6-OMe (**19**), 7-OMe (**20**), 8-OMe (**21**)

Table 5. Characteristics of the long-wavelength absorption bands of PD **18—21** (in CH_2Cl_2) and the δ values

PD	λ^a_{max} /nm	$\varepsilon \cdot 10^{-4}$ /L mol^{-1} cm^{-1}	$M_a{}^{-1}$ /nm	f	σ^a /cm^{-1}	$\gamma_1{}^a$	$\gamma_2{}^a$	F^a	δ
18	706	20.4	685.9	1.02	867	1.57	3.2	0.107	0.1143
19	728	23.4	709.5	0.92	715	1.65	3.8	0.117	0.1098
20	702	25.1	686.9	1.30	776	1.59	3.3	0.108	0.1135
21	712	21.9	691.8	0.99	750	1.62	3.5	0.113	0.1117

Table 6. Characteristics of the long-wavelength fluorescence bands of PD **18—21** (in CH_2Cl_2)

PD	λ^f_{max} /nm	φ (%)	M_f^{-1} /nm	σ^f /cm^{-1}	$-\gamma_1^f$	γ_2^f	F^f	SS_λ cm^{-1}	SS_m cm^{-1}
18	724	8	758.9	832	1.52	2.9	0.104	352	1402
19	744	11	774.1	678	1.59	3.4	0.113	295	1176
20	718	9	753.8	737	1.55	3.0	0.106	317	1292
21	728	10	757.2	708	1.59	3.1	0.109	309	1248

According to the data of quantum-chemical calculations, the π-electron density in the unsubstituted flavylocarbocyanine **13** (R = H) increases ($\Delta q > 0$) after excitation in positions 5, 7, and 8 (Δq = 0.0332, 0.0207, and 0.0078, respectively), and decreases in position 6 ($\Delta q = -0.0063$). In the theory of MO perturbations, the effects of simple substituents on the $\delta\Delta E$ value is described quite satisfactorily[14] by the first term of Eq. (1):

$$\delta\Delta E = \Delta q_X \delta\alpha_X. \qquad (5)$$

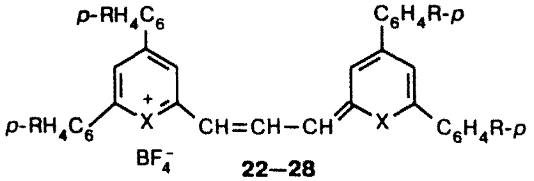
According to the changes in electron density mentioned above and to expression (5), the presence of an electron-donating substituent ($\delta\alpha > 0$) in positions 5, 6, and 8 should result in hypsochromic shifts, while these substituents in positions 6 should lead to bathochromic shifts. The largest shift to the short-wavelength region (Δq_X = max) may be expected when substituents are present in positions 5, while the smallest shift (Δq_X = min) is observed after substitution in positions 8.

It should be noted that the OMe group is able not only to perturb the neighboring atoms due to its inductive effect but also to increase the length of the chromophore due to conjugation.[14] If the latter effect predominates in the molecules of PD **18—21**, the estimations made using Eq. (5), would deviate from experimental results. A comparison of the λ_{max} and M^{-1} values listed in Tables 5 and 6 with the Δq_X values for PD **13** (see above) indicates that the changes in the positions of the maxima and mean positions of the bands in both the fluorescence and absorption spectra that occur after the transition from unsaturated cyanine **13** to methoxy-substituted PD **18—21** are in good agreement with those found from Eq. (5). Thus, the direction in which the bands in the electronic spectra of PD shift after the introduction of a methoxy group into various positions of the heterocyclic residue is mostly determined by the change in the electron density on the neighboring atoms upon excitation.

It may be expected that the value of δ should indicate the trends in the variation of the shapes of the fluorescence and absorption bands for PD **13** and **18—21**, since these compounds incorporate the same atoms, and thus their ν_k values should be close to one another. Thus, according to Eqs. (2)—(4), the shapes of their bands should depend only on δ. In fact, as could be expected judging by the results of quantum-chemical calculations of δ, the introduction of an OMe group in positions 5 and 7 of PD **13** causes broadening of the fluorescence and absorption bands and a decrease in their asymmetry, kurtosis, and degree of structurization, whereas the introduction of this group in positions 6 or 8 leads to the opposite changes (see Tables 5 and 6).

The presence of OMe groups in positions 5 and 7 of a PD molecule also increases the Stokes shifts and decreases the quantum yield of fluorescence, while these groups occurring in positions 6 or 8 lead to the opposite changes. Thus, in the case of PD **13** and **18—21**, not only the variations in the shapes of bands but also the SS_λ, SS_m, and φ values are governed by the VI.

We considered the dependence of fluorescence-spectral properties on the electronic nature of substituents occurring in the same positions of the heterocyclic residues using cyanines **22—28** as examples (Tables 7 and 8).[21]



22—28

X = H (**22**), OMe (**23**), Me (**24**), F (**25**),

Cl (**26**), Br (**27**), NO$_2$ (**28**)

Analysis of the spectral parameters of these compounds (Table 7) shows an unusual redistribution of the

Table 7. Characteristics of the long-wavelength absorption bands of PD **22—28** (in CH_2Cl_2)

PD	λ^a_{max} /nm	$\varepsilon \cdot 10^{-4}$ /L mol^{-1} cm^{-1}	M_a^{-1} /nm	f	σ^a /cm^{-1}	γ_1^a	γ_2^a	F^a
22	730,800	5.89,8.51	739.6	0.78	1176	1.17	2.2	0.064
23	746,824	5.01,8.31	769.5	0.80	1079	1.20	2.0	0.079
24	730,810	5.89,8.91	749.8	0.84	1126	1.18	2.3	0.079
25	730,800	5.89,8.31	741.6	0.79	1150	1.18	2.3	0.070
26	740,815	5.62,7.59	755.5	0.72	1270	1.13	1.8	0.059
27	745,820	5.62,7.59	757.9	0.71	1220	1.14	2.0	0.060
28	760,830	4.17,3.89	759.7	0.60	1370	1.08	1.5	0.054

Table 8. Characteristics of the long-wavelength fluorescence bands of PD **22—28** (in CH_2Cl_2)

PD	λ^f_{max} /nm	φ (%)	M_f^{-1} /nm	σ^f /cm^{-1}	$-\gamma_1^f$	γ_2^f	F^f	SS_λ cm^{-1}	SS_m cm^{-1}
22	840	1.0	869.0	1070	1.12	1.9	0.058	595	2013
23	862	2.0	892.7	987	1.16	2.1	0.063	535	1793
24	849	1.5	877.5	1026	1.14	2.0	0.061	567	1941
25	839	1.5	871.3	1043	1.13	1.9	0.060	581	2007
26	860	0.2	896.3	1135	1.10	1.8	0.056	642	2079
27	865	<0.05	898.2	1096	1.11	1.8	0.057	634	2061
28	880	0.05	905.8	1211	1.05	1.5	0.051	685	2123

absorption intensities for PD **22—28**, namely, the intensity of the vibrational maximum can be either larger or smaller than that of the main maximum, depending on the nature of the substituent. Therefore, while discussing the regularities in the color of pyrylocyanines **22—28**, we shall mostly use the M_a^{-1} values rather than λ^a_{max}.

Attention is attracted by the fact that all substituents, irrespective of their electronic natures, cause bathochromic shifts of the bands in the spectra of the PD under consideration with respect to the bands for unsubstituted cyanine **22** (see Tables 7 and 8).

In terms of their effects on the shapes of the fluorescence and absorption bands of PD **22—28**, substituents can be divided into two groups; the introduction of OMe, Me, or F narrows the bands and increases their intensities, asymmetries, kurtoses, and degrees of structurization, whereas the presence of Br, Cl, or NO_2 exerts the opposite effects. These variations of the σ^a (σ^f), $\gamma_1{}^a$ ($\gamma_1{}^f$), $\gamma_2{}^a$ ($\gamma_2{}^f$), and F^a (F^f) parameters indicate that the shapes of the bands of PD **22—28** are largely determined by the VI (see Eqs. (2)—(4)). Thus, the effect of a "heavy" atom (Cl, Br, NO_2) is not the crucial factor determining the variation of σ, γ_1, γ_2, and F in the spectra of the pyrylocyanines under consideration. This is probably due to the fact that in the molecules of these PD, the substituents do not occupy the key positions of the chromophore and thus they cannot substantially decrease the frequency of the fully symmetrical vibrations ν_k of its atoms. In fact, on going from the chloro-substituted cyanine to bromo-substituted cyanines, the ν_k value decreases by only 16 cm^{-1}, whereas it decreases by 116 cm^{-1} when the S atom in the molecule of PD **4** is replaced by a Se atom.

Apparently, the "heavy" atom effect is significant in the decrease in the φ values for PD **23—28** (compared to those for the unsubstituted cyanine **22**).

The Stokes shifts vary in parallel with the band widths (see Tables 7 and 8). Therefore, the SS_λ and SS_m values are also largely determined by the VI value.

To analyse the electronic effects of substituents, we carried out quantum-chemical calculations of the $M_{calc}{}^{-1}$ and δ values for PD **22—28** (Table 9). The effects of substituents were described in terms of the model of the heteroatom,[22] according to which the electron-donating properties of a substituent are determined by the ability of its unshared electron pair to be involved in conjugation. This ability is specified by the β and α values for the C—R bond and for substituent R, respectively. The electron-withdrawing properties of a substituent, which are determined by its inductive effect, were modeled by varying the α-C atom in position 4′, *i.e.*, by introducing a supplementary inductive parameter.[22] In all cases, it was taken to be $0.1\alpha_R$. The α_R and β_{C-R} values were taken from the literature.[21]

Table 9. Results of quantum-chemical calculations for PD **22—28***

PD	α_R	β_{C-R}	$\alpha_{C(4')}$	β_{C-Ph}	M_{calc}^{-1}/nm	δ
22	—	—	—	0.8	740	0.1723
23	2.0	0.8	0.2	1.0	798	0.1645
24	2.0	0.7	0.2	0.8	744	0.1708
	(2.0)	(0.7)	(0)	(0.8)	(734)	(0.1649)
	(2.0)	(0)	(0.2)	(0.8)	(751)	(0.1779)
25	2.5	0.85	0.25	0.8	743	0.1710
	(2.5)	(0.85)	(0)	(0.8)	(732)	(0.1637)
	(2.5)	(0)	(0.25)	(0.8)	(754)	(0.1793)
26	2.0	0.4	0.2	0.8	748	0.1757
	(2.0)	(0.4)	(0)	(0.8)	(738)	(0.1669)
27	1.5	0.3	0.15	0.8	746	0.1748
	(1.5)	(0.3)	(0)	(0.8)	(739)	(0.1705)
	(1.5)	(0.)	(0.15)	(0.8)	(748)	(0.1766)
28	1.5	1.0	0.15	0.8	765	0.1807
	(1.5)	(1.0)	(0)	(0.8)	(756)	(0.1766)

* Data calculated for the cases in which the substituents exhibit only electron-donating ($\alpha_{C(4')} = 0$) or only electron-withdrawing ($\beta_{C-R} = 0$) properties are given in parentheses.

It can be seen from the data of Table 9 that if a substituent R exhibiting only electron-donating properties ($\alpha_{C(4')} = 0$) is introduced into position 4′ of the unsubstituted pyrylocarbocyanine **22**, hypsochromic shifts and a decrease in the squared variations of the bond orders (see the values in parentheses) should be expected. Substituents exhibiting only electron-withdrawing effects ($\beta_{C-R} = 0$) should cause the opposite changes in the spectra (see Table 9, the values in parentheses). In reality, the predominance of one of these effects over another determines the regularities in the displacements of the fluorescence and absorption bands of substituted PD.

From a comparison of the $M_{calc}{}^{-1}$ values for methyl- and chloro-substituted compounds having identical α_R but different β_{C-R} (see Table 9), one can conclude that the bathochromic shift of the absorption band following the transition from PD **24** to **26** is caused by the fact that the electron-donating properties of Cl are weaker than those of Me, due to a decrease in the effect of conjugation ($\beta_{C-Cl} < \beta_{C-Me}$). However, the methoxy-substituted pyrylocyanine **23** is colored more intensely than the methyl-substituted PD **24**, although $\beta_{C-O} > \beta_{C-Me}$ ($\alpha_{Me} = \alpha_{OMe}$). This is explained by the fact that the introduction of OMe groups into the phenyl ring enhances not only their conjugation with the ring but also the conjugation of the Ph group with the main chromophore of the dye.[20] This fact was taken into account in the quantum-chemical calculations (for compound **23**, $\beta_{C-Ph} = 1$, while for other compounds, $\beta_{C-Ph} = 0.8$). In fact, according to this assumption, PD **23** should have the most intense color and the longest-wavelength fluorescence of the dyes studied.

Of all the substituents considered, the nitro group possesses the strongest electron-withdrawing properties (see Table 9, $\alpha_{C(4')} = 0$). Therefore, of the PD with identical β_{C-Ph}, pyrylocyanine **28** has fluorescence and absorption bands in the longest-wavelength region, as also should be expected from the calculation (see Tables 7—9).

Substantial complications arise when substituents that differ not only in β_{C-R} but also in α_R are compared. For example, the replacement of Cl atoms by Br atoms on the one hand, decreases β_{C-R} and thus weakens the electron-donating properties of the substituent, and on the other hand, enhances the electron-donating properties by decreasing α_R. The calculation implies a hypsochromic shift of bands on going from PD **26** to **27**, *i.e.*, enhancement of the electron-donating properties (weakening of the electron-withdrawing properties) of the substituent. It can be seen from experimental data that the fluorescence and absorption bands of pyrylocyanine **27** are, conversely, shifted bathochromically with respect to those of PD **26**. This contradiction is due to the fact that the changes in the values of λ^a_{max}, M_a^{-1}, λ^f_{max}, and M_f^{-1} for halo-substituted dyes are determined not only by the electronic effects of a substituent, but also by its polarizability,[23] which was not taken into account in the quantum-chemical calculations. The electronic effects of Cl and Br atoms differ only slightly, as can be seen from a comparison of the M_{calc}^{-1} values for compounds **26** and **27**, while the polarizability of the latter is markedly higher. This apparently accounts for the bathochromic shift of the band on going from the chloro-substituted PD to the bromine-containing derivative.

It is even more difficult to draw an unambiguous conclusion about the electronic effects of halogens (or other substituents with different β_{C-R} and α_R) on the positions of bands in the spectra of the PD under consideration, because the variations of these positions can be associated with the extension of the chromophore toward R. This accounts for the fact that all the substituents studied, irrespective of their electronic natures, cause bathochromic shifts of bands of symmetrical pyrylocyanines with respect to those of unsubstituted PD **22**. The band width should be a stricter criterion in this case, since for the compounds under study, it is a function of the VI, the extent of which is determined by the changes in the orders of all the conjugated bands after excitation,[5] irrespective of the direction of the chromophore. In addition, this value depends on the redistribution of the electron density on the atoms in the chromophore, which is caused most of all by the change in the electronic effect of a substituent rather than in its polarizability. The fact that the band of symmetrical dye **22** narrows when OMe or Me groups or an F atom is introduced into its heterocyclic residue indicates that the conjugation effect predominates over the inductive effect. Therefore, these substituents behave as electron donors. Conversely, the broadening of the bands that occurs when the H atoms in the same positions are replaced by Cl or Br atoms or by an NO_2 group indicates that the electron-withdrawing properties of these substituents predominate (the inductive effect prevails over conjugation).

Thus, the fluorescence-spectral properties of PD can be controlled over a broad range by making diverse changes in the structures of the heterocyclic residues (isomerism, annelation, heteroatom replacement, introduction of substituents of various natures into different positions of the nucleus). The regularities established in the present study allow one to make these changes in a target-directed way.

References

1. A. A. Ishchenko, *Usp. Khim.*, 1991, **60**, 1708 [*Russ. Chem. Rev.*, 1991, **60** (Engl. Transl.)].
2. T. Clark, *A Handbook of Computational Chemistry*, Wiley and Sons, New York, 1985.
3. A. I. Tolmachev, A. A. Ishchenko, M. A. Kudinova, V. V. Kurdyukov, S. V. Sereda, *Dyes and Pigments*, 1991, **17**, 71.
4. A. A. Ishchenko, N. A. Derevyanko, V. M. Zubarovskii, and A. I. Tolmachev, *Teor. Eksp. Khim.*, 1984, **20**, 443 [*Theor. Exp. Chem.*, 1984, **20** (Engl. Transl.)].
5. A. A. Ishchenko, *Stroenie i spektral'no-lyuminestsentnye svoistva polimetinovykh krasitelei* [*Structure and Luminescence Spectral Properties of Polymethine Dyes*], Naukova Dumka, Kiev, 1994, 232 pp. (in Russian).
6. A. A. Ishchenko, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1227 [*Russ. Chem. Bull.*, 1994, **43**, 1161 (Engl. Transl.)].
7. A. A. Ishchenko, N. A. Derevyanko, and V. A. Svidro, *Optika i Spektroskopiya* [*Optics and Spectroscopy*], 1992, **62**, 110 (in Russian).
8. G. G. Dyadyusha, A. A. Ishchenko, and I. L. Mushkalo, *Zhurn. Nauchn. i Prikl. Fotogr. i Kinematogr.* [*J. of Scientific and Applied Photography and Cinematography*], 1981, **26**, 174 (in Russian).
9. M. A. Kudinova, N. A. Derevyanko, G. G. Dyadyusha, A. A. Ishchenko, and A. I. Tolmachev, *Khim. Geterotsikl. Soedin.*, 1980, 898 [*Chem. Heterocycl. Compd.*, 1980 (Engl. Transl.)].
10. A. I. Tolmachev, N. A. Derevyanko, and A. A. Ishchenko, *Khim. Geterotsikl. Soedin.*, 1982, 1178 [*Chem. Heterocycl. Compd.*, 1982 (Engl. Transl.)].
11. S. V. Sereda, A. A. Ishchenko, M. A. Kudinova, V. V. Kurdyukov, and A. I. Tolmachev, *Zh. Strukt. Khim.*, 1992, **33**, 139 [*Russ. J. Struct. Chem.*, 1992, **33** (Engl. Transl.)].
12. V. G. Plotnikov, *Usp. Khim.*, 1980, **49**, 327 [*Russ. Chem. Rev.*, 1980, **49** (Engl. Transl.)].

13. A. I. Tolmachev, N. A. Derevyanko, and A. A. Ishchenko, *Khim. Geterotsikl. Soedin.*, 1982, 1173 [*Chem. Heterocycl. Sompd.*, 1982 (Engl. Transl.)].
14. M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975.
15. A. I. Tolmachev, M. Yu. Kornilov, L. M. Shulezhko, and A. V. Turov, *Teor. Eksp. Khim.*, 1975, **11**, 556 [*Theor. Exp. Chem.*, 1975, **11** (Engl. Transl.)].
16. A. A. Ishchenko, *Optika i Spektroskopiya* [*Optics and Spectroscopy*], 1994, **77**, 771 (in Russian).
17. A. I. Tolmachev, G. G. Dyadyusha, E. F. Karaban, A. A. Ishchenko, and N. A. Derevyanko, *Khim Geterotsikl. Soed.*, 1978, 739 [*Chem. Heterocycl. Compd.*, 1978 (Engl. Transl.)].
18. A. A. Ishchenko, V. A. Svidro, and N. A. Derevyanko, *Dyes and Pigments*, 1989, **10**, 85.
19. E. D. Sych, *Ukr. Khim. Zh.* [*Ukrainian Chem. J.*], 1959, **25**, 767 (in Russian).
20. I. M. Gavrilyuk, A. A. Ishchenko, M. A. Kudinova, and A. I. Tolmachev, *Khim. Geterotsikl. Soedin.*, 1983, 304 [*Chem. Heterocycl. Compd.*, 1983 (Engl. Transl.)].
21. I. I. Boiko, N. A. Derevyanko, A. A. Ishchenko, T. A. Markina, and A. I. Tolmachev, *Khim. Geterotsikl. Soedin.*, 1986, 1607 [*Chem. Heterocycl. Compd.*, 1986 (Engl. Transl.)].
22. A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, J. Wiley and Sons, New York, 1961.
23. C. N. R. Rao, *Elektronnye spektry v khimii* [*Ultra-Violet and Visible Spectroscopy. Chemical Applications*], Mir, Moscow, 1964, 264 pp. (Russ. Transl.)

Received December 5, 1995;
in revised form April 18, 1996