Russian Chemical Bulletin, Vol. 43, No. 7, July, 1994 1161

The length of the polymethine chain and the spectral-luminescent properties of symmetrical cyanine dyes

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The general characteristics that relate the length of the polymethine chain of symmetrical cyanine dyes to their spectral-luminescent properties depending on the electron-donor character of the heterocycles and the nature of the solvent are formulated. For various types of symmetrical cyanines, the Stokes shifts decrease with the elongation of the polymethine chain due to weakening of the vibronic interactions. The vinylene shifts of the band maxima are essentially constant and fall within the range 100 to 130 nm depending on the nature of the heterocycles and the solvent. When the polymethine chain elongates the fluorescence quantum yields first increase and then decrease. The greater the effective length of the heterocycle the stronger the decrease. The fluorescence decay occurring when the polymethine chain gets longer is associated with intensification of the internal conversion. For symmetrical cyanines, the changes in the shapes of the electronic bands (their width, asymmetry, excess, and fine structure) as the chain elongates are governed by the competing effects of the vibronic and intermolecular interactions. The former decrease as the chain lengthens, causing the narrowing of the absorption bands for the lower vinylogs. On the other hand, the latter increase as chain lengthens, which leads to broadening of the bands for the higher vinylogs. The higher the solvent nucleophilicity and the greater the deviation of the electron-donor ability of the heterocycle from the average value the greater the broadening. Any elongation of the polymethine chain of symmetrical cyanines causes only narrowing of the bands and an increase in the asymmetry, excess, and structuring in the fluorescence spectra, which, unlike the absorption spectra, is independent of the electron-donor character of the heterocycles and the nature of the solvent. These effects are caused by the fact that, in contrast to absorption, changes in the shape of emission bands with increasing chain length are governed predominantly by vibronic rather than by intermolecular interactions.

Key words: cyanine dye; polymethine chain; spectral-luminescent properties; vibronic and intermolecular interactions; internal conversion.

The polymethine chain is the most important structural factor of organic dyes.[1—4] Lengthening the polymethine chain is one of the main methods for the preparation of practically important deeply colored compounds.[1—4] The general characteristics of the effect of the length of the polymethine chain on the spectral-luminescent properties of dyes as a function of the nature of the heterocycles and the solvent must be established for their directed synthesis. In the present work the absorption and fluorescence spectra of vinylog series of symmetrical cyanine polymethine dyes (PD)* **1—30** [2—7] have been studied.

The dyes differ in the structure and electron-donor ability Φ_0 of the heterocyclic rings in solvents with different polarity. The polymethines studied are based on heterocycles with medium (**1—5** and **14—16**),[4,5] strong (**6—13**),[4] and weak (**17—30**)[6,7] electron-donating ability.

The quantitative evaluation of the changes in the electronic spectra of the dyes studied was carried out by mathematical processing of their long-wave absorption bands according to the method of moments.[8] This allowed one to obtain important additional information about the average position of the bands M_a^{-1} (M_f^{-1}), the strength of the oscillator f, the width σ^a (σ^f), and coefficients of asymmetry $\gamma_1{}^a$ ($\gamma_1{}^f$), excess $\gamma_2{}^a$ ($\gamma_2{}^f$), and fine structure of the bands F^a (F^f)[8] (indices a and f relate to absorption and fluorescent spectra, respectively) in addition to the usual spectral parameters, *viz.*, the maximum of the band λ^a_{max}(λ^f_{max}) and its extinction. The values of Stokes shifts ΔS_λ and ΔS_M were also calculated from λ^a_{max}, λ^f_{max} and M_a^{-1}, M_f^{-1}, the wavelengths at the intersection point of the absorption and fluorescent spectra (λ_e) and the fluorescence quantum

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* Abbreviations: IMI is intermolecular interactions; PD is polymethine dye; DMF is dimethylformamide.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1227—1239, July, 1994.

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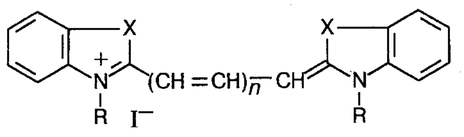
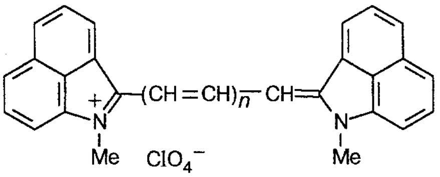
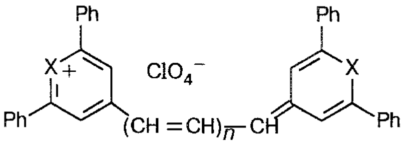


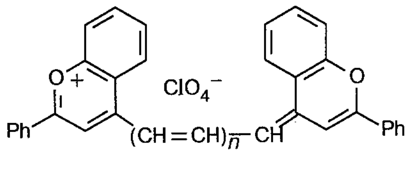
1–5: X = C(Me)$_2$, R = Me, n = 1÷5
6–10: X = S, R = Et, n = 1÷5
11–13: X = NPh, R = Ph, n = 1÷3



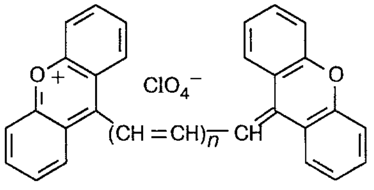
14–16: n = 1÷3



17–20: X = O, n = 0÷3
21–24: X = S, n = 0÷3



25–27: n = 0÷2



28–30: n = 1÷3

yields (ϕ). It is noteworthy that λ_e for PD is often identified in literature with the frequency or wavelength of the 0—0 λ_{00} transition.[9] Since the four-level scheme of electron states is realized for the majority of cyanines,[10] these values do not coincide, although one may consider $\lambda_e \approx \lambda_{00}$ for small Stokes shifts.

Experimental

The ϕ values were measured relative to the quantum yields of ethanolic solutions of PD **1—3**.[11]

The moments in the absorption spectra were determined in coordinates ε/ν, ν, and in the fluorescent spectra, in coordinates W/ν^4, ν. The law of mirror symmetry of these spectra must be most rigorously fulfilled for these coordinates.[10]

Spectral-luminescent characteristics of PD **1—30** in weakly polar dichloromethane, moderately polar ethanol, and strongly polar acetonitrile and DMF are presented in Figs. 1—8.

Results and Discussion

It should be noted that the determination of the moments of the bands in the coordinates mentioned imposes considerably heavier demands on the measurement of the intensities at the ends of the fluorescence bands than those of the absorption spectra. This is caused by the fact that moments can be reliably determined when the intensity at the band maximum is at least two orders of magnitude higher than the intensity at its minimum.[8] This condition must be primarily met for the flattened descending end of the spectrum,[8] which is the short-wave end in absorption and the long-wave end in fluorescence. For absorption spectra, division of the extinction value into the frequency at this end results in an increase in the depth of the spectrum measurement, since the maximum values of intensity are divided into the lower frequency values, and

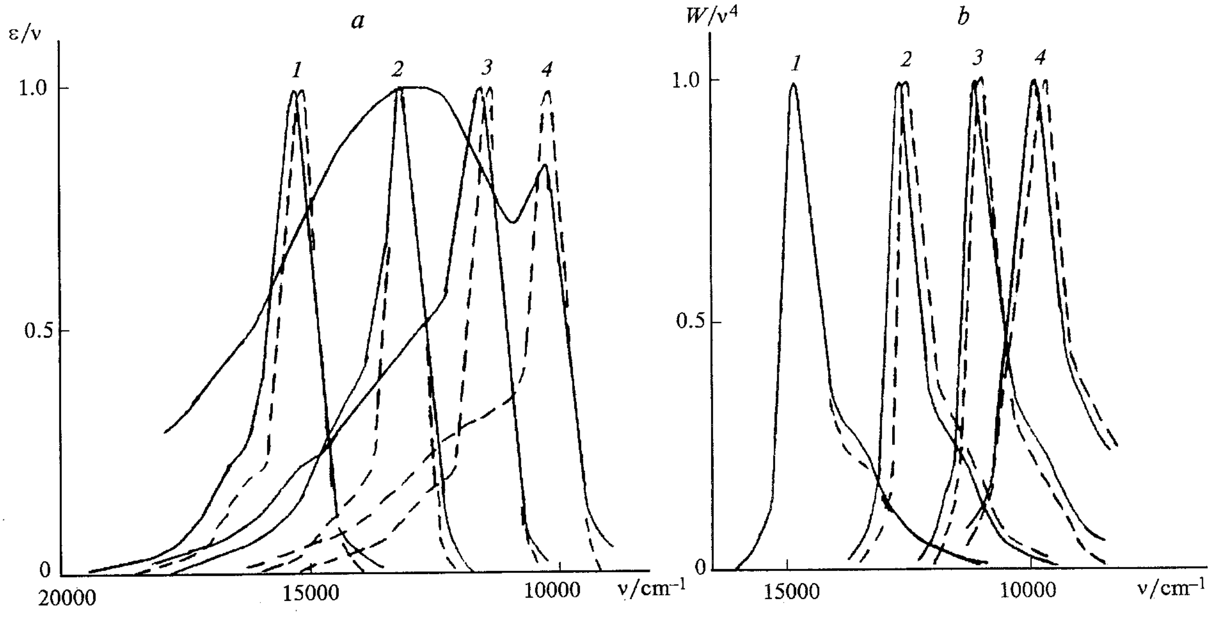


Fig. 1. Absorption (*a*) and fluorescent (*b*) spectra for solutions of PD **7** (curve *1*), **8** (*2*), **9** (*3*), and **10** (*4*) in CH$_2$Cl$_2$ (dotted lines) and DMF (solid lines).

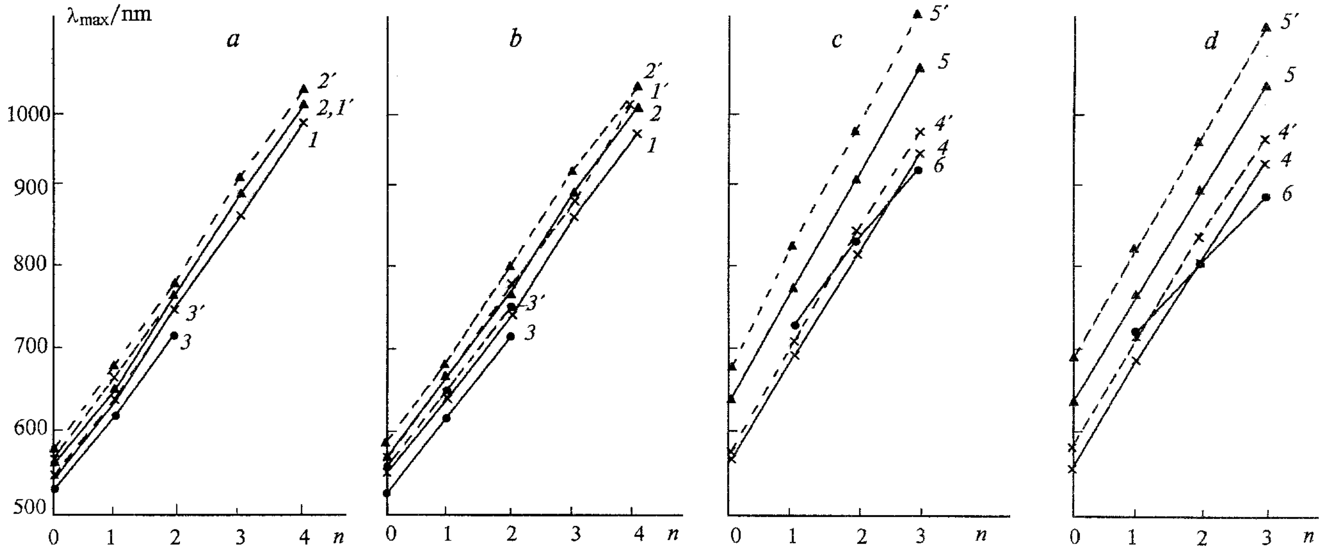


Fig. 2. Dependence of the maximum of the long-wave absorption (*1—6*) and fluorescent (*1′—5′*) bands for PD **1—13**, **17—24**, and **28—30** on the polymethine chain length in CH_2Cl_2 (*a*, *c*), DMF (*b*), and acetonitrile (*d*): PD **1—5** (curve *1*, *1′*), **6—10** (*2*, *2′*), **11—13** (*3*, *3′*), **17—20** (*4*, *4′*), **21—24** (*5*, *5′*), **28—30** (*6*).

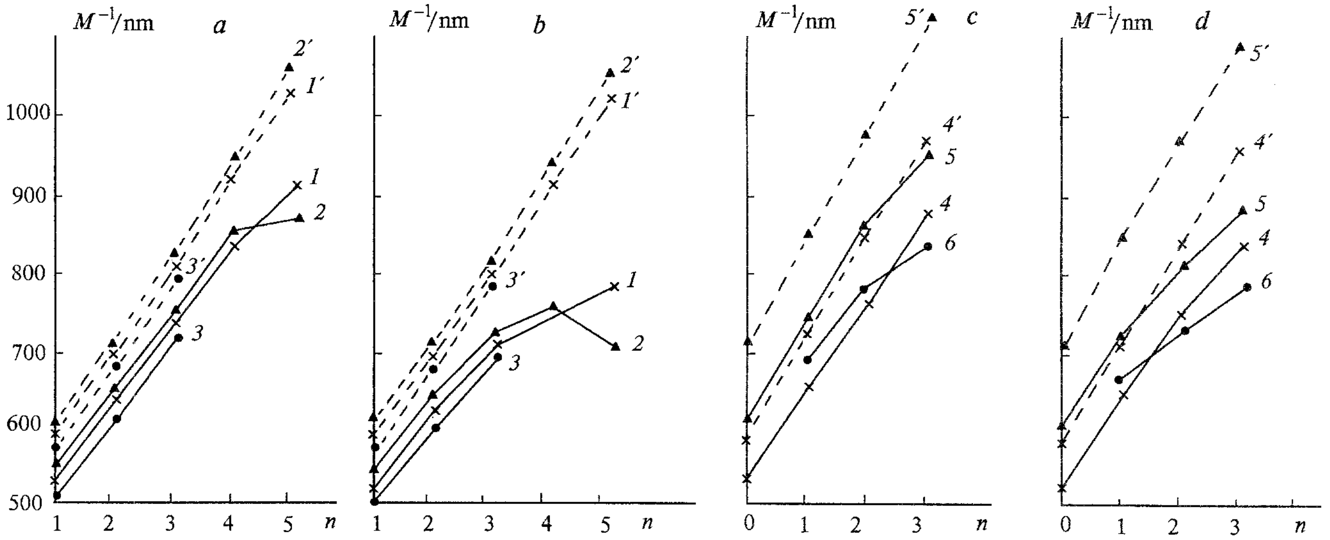


Fig. 3. Dependence of the average position of the long-wave absorption (*1—6*) and fluorescent (*1′—5′*) bands for symmetrical PD **1—13**, **17—24**, and **28—30** on the length of the polymethine chain. Designations for dyes and solvents are the same as in Fig. 2.

the minimum values are divided into the greater frequency values. For fluorescent spectra, this operation, on the contrary, sharply decreases the depths of measurements (W_{max} is divided into the greater frequency values, and W_{min} is divided into the lower ones). Moreover, they are divided not into ν but into ν^4. Therefore, fluorescent spectra must be registered considerably more deeply than absorption spectra, which is not always possible even for dyes with high quantum yields, especially in the range of $\lambda > 800$ nm where the sensitivity of the photodetector is strongly reduced.[12] The use of laser excitation and the PMT-83 cooling system in an SDL-1 spectrophotometer allowed us to measure the fluorescence spectra of dyes **1—30** in the range 400—1150 nm more than two orders of magnitude in height in coordinates W/ν^4 and to achieve the same accuracy in the determination of the moments as for the absorption spectra.

The influence of the length of the polymethine chain on absorption spectra of symmetrical PD

As can be seen from Figs. 1, *a* and 2, lengthening the polymethine chain by one vinylene group in all of the series of the dyes studied results in a regular bathochromic shift of λ^a_{max} by a value close to 100 nm. Changes in the structure and electron-donor ability of the heterocycles have a slight effect on this value. It is almost independent of the nature of the solvent.

Another situation is observed for vinylene shifts ΔM_a^{-1} calculated from the average positions of the absorption bands (see Fig. 3). An increase in n usually results in a decrease in ΔM_a^{-1}, especially in polar solvents. For example, this value decreases to 53.8 nm in acetonitrile on going from xanthylodicarbocyanine **29** to xanthylotricarbocyanine **30**, and even negative values of ΔM_a^{-1} are achieved for indo- and thiacyanines when n increases from 4 to 5 (see Fig. 3, *c, d*). This drastic change in the average (not maximum) positions of bands, when the polymethine chain is lengthened is caused by a considerable change in the shape of the absorption bands (see Fig. 1, *a*), to which ΔM_a^{-1}, which reflects the average position of a band, is rather sensitive.

The analysis of the shape of bands, especially of their widths, in the vinylog series of PD **1—30** reveals some serious contradictions to previous conclusions[13] about their change with the increase in n. It can be seen from Fig. 4 that the conclusion[13] that the absorption bands become narrower as the polymethine chain lengthens is not true for any series of dyes. This occurs only to tricarbocyanines for cyanines **1—5** and **14—16** containing heterocycles with medium electron-donor ability in weakly polar dichloromethane (see Fig. 4, *a*, curve *1*). The band narrowing is especially great for the increase in n from 1 to 2: the band width in dichloromethane decreases by 217 cm^{-1} on going from compound **1** to **2** and by 91 cm^{-1} on going from **14** to **15**. Lengthening the polymethine chain by one more vinylene group causes the bands to become only 44 and 11 cm^{-1} narrower in these series of dyes, respectively, and a further increase in n is accompanied by considerable broadening of the bands (see Fig. 4, *a*). The width of the band reaches 113 cm^{-1} on going from indotri- to indotetracarbocyanine and 392 cm^{-1} on going from indotetra- to indopentacarbocyanine. For dyes **6—10** (see Fig. 4, *a*, curve *2*) where the indolium ring is replaced by a more electron-donor benzothiazolium ring, the absorption bands are narrowed only as n increases from 1 to 2, and its value is considerably lower (118 cm^{-1}) than that for the corresponding indocyanines (see Fig. 4, *a*). The transition from tri- to tetra- and then to pentacarbocyanines is accompanied by relatively greater broadening than for the similar series of compounds **3—5**. In the series of benzimidazolocyanines **11—13** (see Fig. 4, *a*, curve *3*) containing more electron-donor terminal groups, bands do not narrow for any polymethine chain elongation.

Now let us analyze the influence of a negative deviation of Φ_0 of the heterocycles from the average value on the change in σ^a as n increases. It is seen from Fig. 4, *c* that for PD **17—30** containing fewer electron-donor rings than cyanines **1—5**, the transition from carbo- to dicarbo- and then to tricarbocyanines in dichloromethane is accompanied not by the narrowing but by the broadening of the absorption bands as for the series of dyes with the strong electron-donor heterocycles, benzothiazolium and benzimidazolium. A further decrease in Φ_0 of the terminal groups relative to the mean value enhances these effects. As the electron-donor ability of heterocycles decreases in the series pyrilo-, flavilo-, and xanthylocyanines[7] σ^a increases by 10, 25, and 123 cm^{-1}, respectively, in dichloromethane on going from carbo- to dicarbocyanines. As n increases from 1 to 2 the absorption bands broaden more strongly for thiopyrilocyanines **22** and **23** than for their oxygen analogs **18** and **19** (see Fig. 4, *c*), because Φ_0 for thiopyrilium rings are lower than that for pyrilium rings.[6] Similar tendencies in the change in σ^a during polymethine chain elongation are also observed for higher vinylogs of these PD (see Fig. 4, *a*). They are not always so distinct for the transition from monomethine- to carbocyanines because the spectral properties of PD (for PD with $n = 0$) may be strongly affected by the effects associated with the arrangement of the nearby rings, for example, steric hindrances[14] and nonvalent atomic interactions.[15]

The width (and, in general, the shape) of electron absorption bands of organic dyes is primarily determined

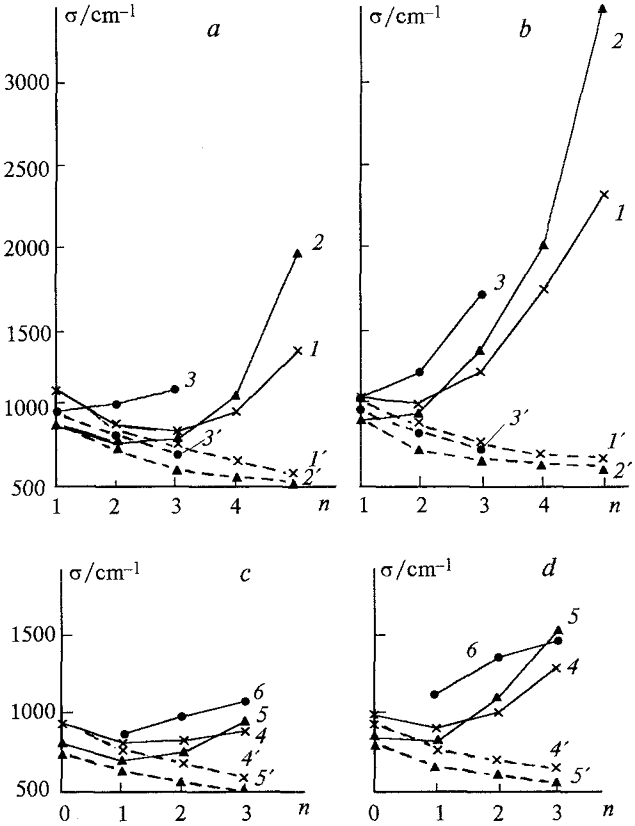


Fig 4. Dependence of the width of the long-wave absorption (*1—6*) and fluorescent (*1′—5′*) bands for PD **1—13**, **17—24**, and **28—30** on the polymethine chain length. Designations for dyes and solvents are the same as in Fig. 2.

by vibronic interactions and IMI.[16] Sometimes a band may include the superposition of two or more bands when there is a mixture of stereoisomers.[14]

Vibronic interactions in PD are primarily associated with changes in the lengths of the C—C bonds in the conjugation chain as the result of electron excitation. Therefore, the value δ of the quadratic changes in the bond orders during excitation may be successfully used to quantitatively estimate the changes in the degree of vibronic interactions in PD molecules:[17]

$$\delta = \sqrt{\sum_{i=1}^{m} (P^{*} - P^{0})_i^{2}} \ ,$$

where i is the bond number, and m is the number of bonds.

It has been shown[16] that δ and, therefore, the vibronic interactions as well, must decrease as the polymethine chain lengthens in symmetrical PD with conjugated bonds in the polymethine chain. In turn, this indicates that narrowing of the electronic bands might be expected as n increases. However, according to the data presented above, if this is the case for the absorption spectra, then it occurs only for the initial lengthening of the polymethine chain (see Fig. 4, *a, c*). Therefore, the changes in the vibronic interactions as n increases should also be analyzed in terms of a more complicated model. One such model results from the fact that it is possible for the bond orders of the polymethine chain to alternate from the center to the ends for symmetrical PD whose heterocycles significantly differ from the average electron-donor ability.[18] The terminal bonds of the polymethine chain must have a lower order and the central bonds must have a higher order for cyanines with strong electron-donor residues ($\Phi_0 > 45°$). The reverse distribution of the bond orders is assumed for PD with weak electron-donor rings ($\Phi_0 < 45°$). In the case of cyanines with average electron-donor heterocycles ($\Phi_0 = 45°$), complete conjugation must take place as in the case of benzene, *i.e.*, an ideal polymethine state is realized.[18] Therefore, equal values of the resonance integrals β may be used for all of the bonds of these PD, whereas for the dyes with heterocycles whose electron-donor ability is higher or lower than 45° the values $\beta < 1$ for bonds of the polymethine chain with a lower order and $\beta > 1$ for bonds with a higher order must be used.

It can be suggested that alternation of bonds in the chain of symmetrical dyes enhances vibronic interactions and, hence, broadens the absorption bands in dichloromethane as the polymethine chain lengthens for higher vinylogs of PD and for all cyanines based on benzimidazole (see Fig. 4, *a*). To test this suggestion, we performed quantum-chemical calculations (using a simple MOC method with various amplitudes of β alternation in the chain) of cations **11—13**, whose band broadening as n increases is the most significant. The values of β in the rings and the parameters of the heteroatoms were unchanged in the calculations. The numerical values of the parameters have been determined previously.[19] Since we were interested not in the absolute values of the calculated parameters but in their tendencies to change, the influence of the phenyl groups was not taken into account for simplicity. The results of the quantum-chemical calculations of the absorption maxima λ^{a}_{t}, the strengths of the oscillators f_t, and the quadratic changes in the bond orders during excitation are presented in Table 1 for **11—13**.

It can be seen from Table 1 that increasing the β alternation in the polymethine chain retards the decrease in δ as n increases. The increase in this value for higher vinylogs of benzimidazolocyanines begins only at huge amplitudes of β (±26 %). For the whole series of dyes **11—13**, the quadratic changes in the bond orders increase for higher degrees of the β alternation (amplitude ±44 %). Such a strong alternation of bonds is atypical not only of symmetrical PD but of polyenes as well.[13] In fact, for cyanines **11—13** the first and second vinylene shifts must decrease to 77 and 36 nm, respectively, for the amplitude of 26 %, and to 59 and 12 nm for 44 %. These data contradict the experiment, because the values of the shifts mentioned are not lower than 90 nm either for $\lambda^{a}_{\max}$ or for M_a^{-1} (see Figs. 2 and 3). In addition, the increase in n for these amplitudes must

Table 1. Results of the quantum-chemical calculations for dyes **11—13** with different amplitudes of the β alternation in the polymethine chain

β_{C-C}	$\beta_{C=C}$	n	λ^{a}_{t}/nm	f_t	δ
1.00	1.00	1	371	1.74	0.1785
		2	465	2.12	0.1470
		3	563	2.51	0.1253
0.98	1.02	1	368	1.75	0.1755
		2	462	2.10	0.1455
		3	553	2.51	0.1260
0.96	1.04	1	366	1.74	0.1728
		2	458	2.08	0.1443
		3	544	2.50	0.1271
0.94	1.06	1	364	1.74	0.1704
		2	455	2.05	0.1435
		3	536	2.48	0.1287
0.92	1.08	1	362	1.73	0.1684
		2	452	2.01	0.1431
		3	528	2.44	0.1307
0.74	1.26	1	357	1.49	0.1658
		2	434	1.41	0.1563
		3	470	1.69	0.1616
0.56	1.44	1	365	1.05	0.1800
		2	424	0.62	0.1809
		3	436	0.65	0.1880
0.48	1.52	1	372	0.84	0.1866
		2	421	0.35	0.1888
		3	427	0.34	0.1937

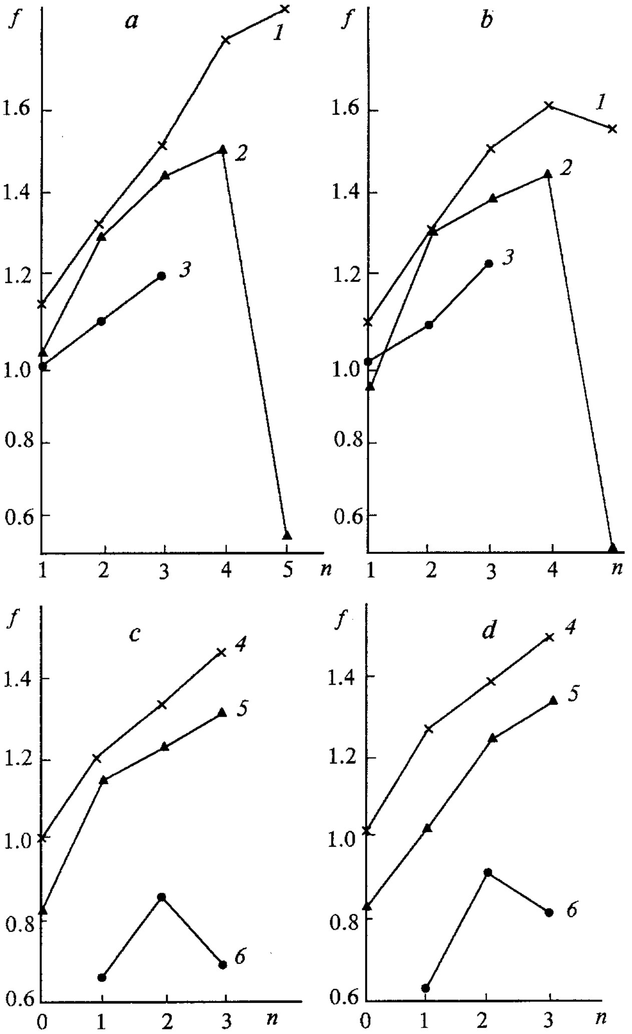


Fig. 5. Dependence of the oscillator strength (*1—6*) for PD **1—13**, **17—24**, and **28—30** on the polymethine chain length. Designations for dyes and solvents are the same as in Fig. 2.

result in a decrease in the oscillator strength, which also does not correlate with the changes in the experimental *f* values. One can draw the conclusion based on the comparison of the calculated and observed values of the vinylene shifts that the amplitudes of β alternation are in the range from 0 to ±2 % for benzimidazolocyanines, *i.e.,* they are rather insignificant. This conclusion agrees well with the data of X-ray analysis of this class of dyes. It follows from these data that the carbon—carbon bonds in their polymethine chains are almost conjugated.[20]

As can be seen from Table 1, this weak alternation of bonds cannot cause an increase in the vibronic interactions and, hence, a broadening of the absorption bands of **11—13** as the polymethine chain lengthens (δ values decrease).

Similar quantum-chemical calculations of thiopyrilocyanines containing weak electron-donor heterocycles show that the amplitude of the alternation of the chain bonds for PD **21—24** is of the same order as for **11—13**. This conclusion also agrees well with the data of X-ray analysis.[15]

Therefore, the previous conclusion about the weakening of vibronic interactions as the polymethine chain lengthens[16] holds true for symmetrical PD, including those, whose rings have different electron-donor abilities. It thus follows that the increase in δ^a as *n* increases in the cases noted above is caused by other factors.

In many cases, broadening of the absorption bands (for example, for all benzimidazolocyanines **11—13** and as *n* increases from 3 to 4 and 5 for indocyanines, from 2 to 3 for thiacyanines, and from 1 to 2 for pyrilocyanines and their analogs) results not in decreases in *f*, $\gamma^a{}_1$, $\gamma^a{}_2$ and F^a, as should be expected for the enhancement of vibronic interactions,[17] but, on the contrary, in their increase (see Figs. 5—8). This inconsistency (in the change in the width of absorption bands and these coefficients) indicates that the change in δ^a as the polymethine chain lengthens is determined not only by vibronic interactions but by other factors as well.

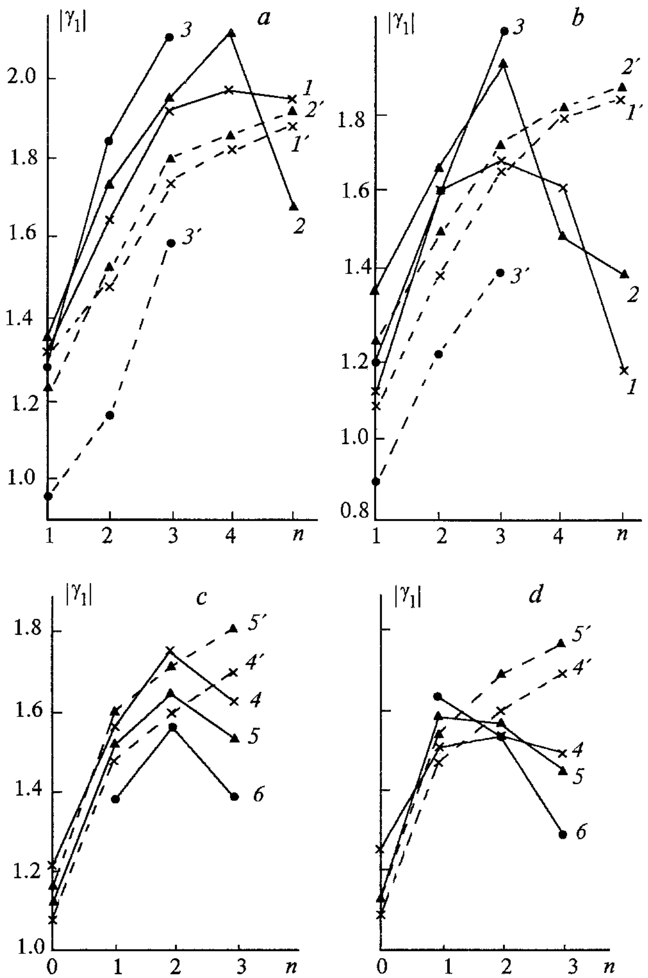


Fig. 6. Dependence of the asymmetry coefficient of the long-wave absorption (*1—6*) and fluorescent (*1′—5′*) bands for PD **1—13**, **17—24**, and **28—30** on the polymethine chain length. Designations for dyes and solvents are the same as in Fig. 2.

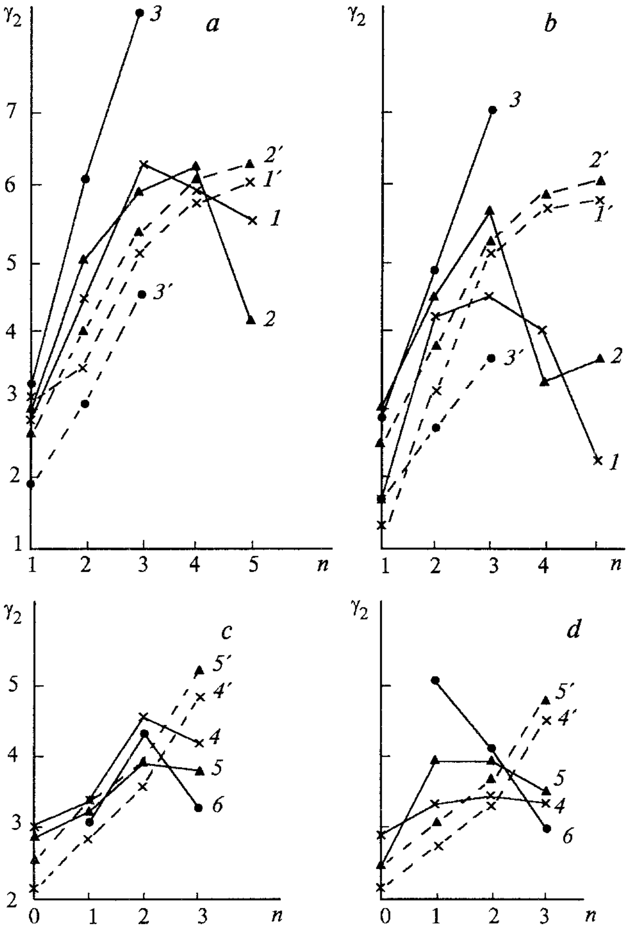


Fig. 7. Dependence of the excess coefficient of the long-wave absorption (*1—6*) and fluorescent (*1'—5'*) bands for PD **1—13**, **17—24**, and **28—30** on the polymethine chain length. Designations for dyes and solvents are the same as in Fig. 2.

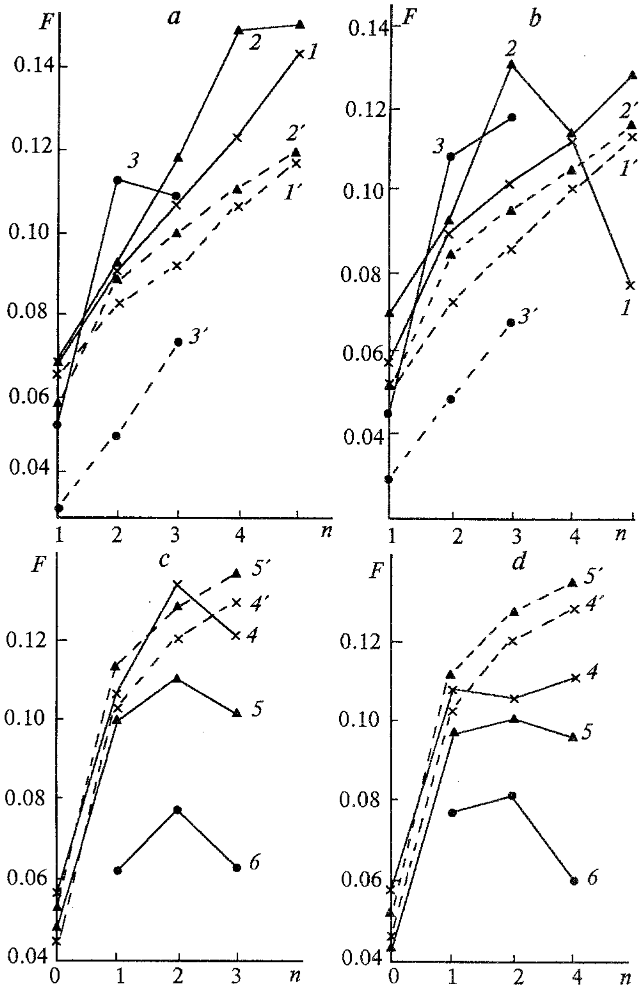


Fig. 8. Dependence of the fine structure coefficient of the long-wave absorption (*1—6*) and fluorescent (*1'—5'*) bands for PD **1—13**, **17—24**, and **28—30** on the polymethine chain length. Designations for dyes and solvents are the same as in Fig. 2.

^{1}H NMR spectra of cyanines **1—3**, **6—8**, **11—13**, and **17—19** were studied in CD_2Cl_2, acetonitrile, and DMF to check the possibility of explaining the broadening of the absorption bands of the PD studied by the existence of a mixture of stereoisomers. The values of the spin coupling constants of the protons of the polymethine chain were within the range 12.5—14 Hz for all of these compounds in the solvents mentioned. These values indicate[14] that PD **1—30** exist only as «*all-trans*» isomers independently of the polymethine chain length and electron-donor ability of the heterocycles, which is typical of cyanines bearing no substituents in the chain. Therefore, the broadening of the absorption bands of the considered dyes with the increase in *n* is not associated with stereoisomery, and may be assigned only to IMI of a dye with a solvent, which, unlike vibronic interactions, should increase as the polymethine chain lengthens. IMI exert the most significant effect on δ^a of bands in polar media (see Fig. 4). This conclusion follows from the fact that the narrowing of bands as *n* increases is considerably weaker and the broadening is much stronger in polar solvents. For example, the transition from **1** to **2** causes δ^a to decrease by 98 and 53 cm^{-1} in ethanol and DMF, respectively, whereas it decreases by 217 cm^{-1} in dichloromethane. The increase in *n* from 2 to 3 in the first two solvents, unlike the latter, is accompanied by broadening of the absorption bands.

Solvation effects are enhanced when the electron-donor ability of the heterocycles of PD deviates in either direction from the mean value. Indeed, for cyanines **6—10** whose rings have greater Φ_0 than those of compounds **1—5**, δ^a is almost unchanged in ethanol on going from carbo- to dicarbocyanine, and there is no narrowing of bands at all in DMF as the polymethine chain lengthens (see Fig. 4, *b*). For PD **11—13**, containing even more electron-donor heterocycles, increasing *n* in all of the solvents causes the broadening of only those bands, whose value significantly exceeds the similar

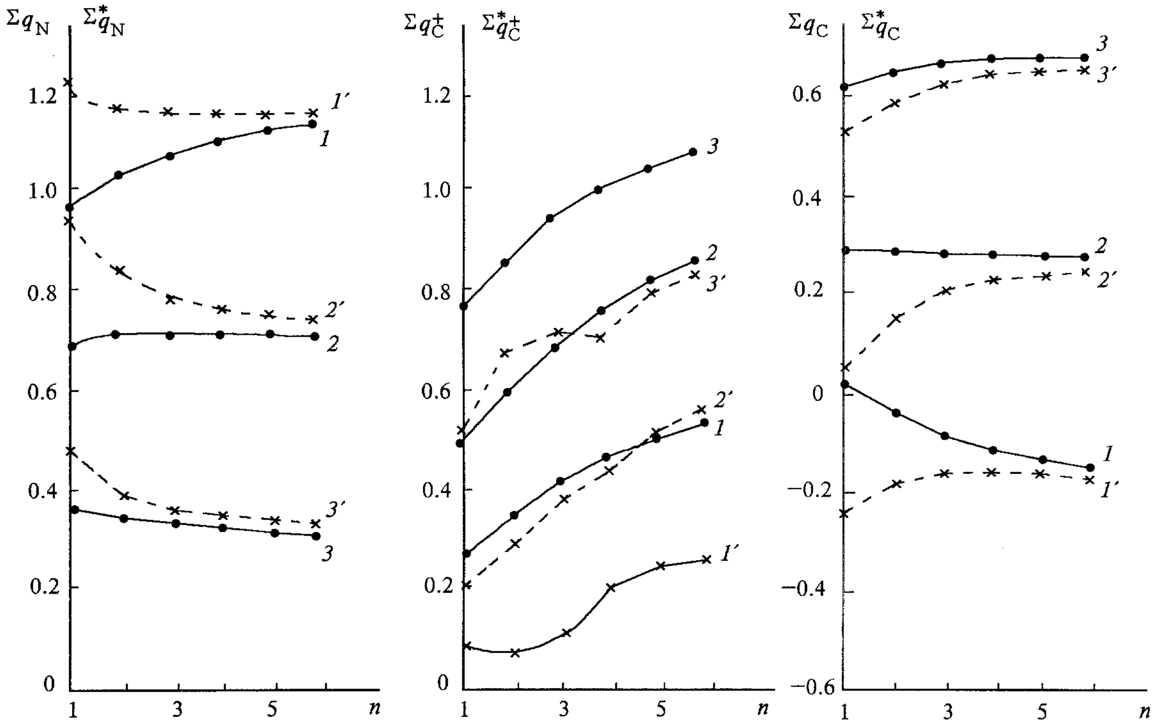


Fig. 9. Dependence of Σq_N, Σq^+_C, Σq_C (curves *1—3*) and $\Sigma^* q_N$, $\Sigma^* q^+_C$, $\Sigma^* q_C$ (curves *1'—3'*) on the polymethine chain length and electron-donor ability of terminal groups: for α_N = 2, 1 and 0.5 (curves *1, 1'*; *2, 2'*; and *3, 3'*, respectively).

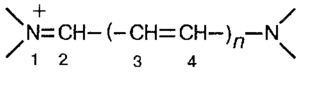
value for the corresponding indo- and thiacyanines, and increases when dichloromethane is replaced by ethanol and DMF.

For pyrilocyanines **17—20**, whose rings possess lower Φ_0 than those of indolium, the transition from carbo- to dicarbocyanine, unlike PD **1** and **2**, is accompanied by broadening of the absorption bands when dichloromethane is replaced by acetonitrile (see Fig. 4, *d*). The broadening regularly increases as the electron-donor ability of the heterocycles, further decreases during both their annealing and the displacement of their oxygen atoms by sulfur (see Fig. 4, *d*). For example, the increase in *n* from 1 to 2 broadens the absorption band in acetonitrile for pyrilo-, flavilo-, xanthylo-, and thiopyrilocyanines by 110, 180, 217, and 234 cm^{-1}, respectively.

Increasing the polarity of the solvent also causes hypsochromic shifts of the absorption bands. This is especially noticeable in the change in $M^{-1}{}_a$ (see Fig. 3). There is a tendency for the hypsochromic shifts of the average positions of the absorption bands to increase (this can be seen most distinctly in the calculations of the solvatochromic shifts in cm^{-1}) as *n* increases and when the heterocycles deviate from the average electron-donor ability.[16]

The nature of the solvent has a significant effect on the intensity and shape of absorption bands. This effect is sharply enhanced as the polymethine chain lengthens. The transition from dichloromethane to more polar solvents results in a drop in intensity, a decrease in the asymmetry of a band, and an increase in its flattened and blurred character (decrease in *f*, $\gamma^a{}_1$, $\gamma^a{}_2$, and $F^{\,a}$). There is also a tendency for this effect to increase when Φ_0 of the heterocycles deviates from the average electron-donor ability (see Figs. 5—8).

Since PD are charged compounds, their molecules can be subjected to specific solvation by polar molecules of solvents due to Coulomb interactions,[21] which depend significantly on the charge distribution in the cations of the dyes. To analyze the change in this distribution as a function of the electron-donor ability of the terminal groups (heterocyclic rings) and the polymethine chain length, the quantum-chemical calculations of the charge distribution in model dyes of the general formula



were performed where N are terminal heterocyclic groups, whose electron-donor ability was varied by changing their Coulomb integral α_N from 2 to 0 (Fig. 9). The calculations were performed by a simple MOC method. The values $\beta_{CN} = \beta_{CC} = \beta$ and $\alpha_C = 0$ for all α_N values.

The net charges at the terminal groups Σq_N (this value is also the net positive charge on the rings) and

Σq_C for the polymethine chain, and the net positive charge Σq^+_C for the polymethine chain were calculated. For the considered series of model compounds, the value $\alpha_N = 1$ corresponds to terminal heterocyclic groups of average electron-donor ability, $\alpha_N > 1$ corresponds to weak ability, and $\alpha_N < 1$ corresponds to strong electron-donor ability. The net charge of a cation ($\Sigma q_N + \Sigma q_C$) remains equal to +1 as the Coulomb integrals of the model dyes vary. However, the charge is nonuniformly distributed in the cation, and is primarily localized either at the terminal groups or in the polymethine chain depending on α_N. Polar molecules of a solvent must solvate the sites with the most concentration of the charge especially strongly. It follows from Fig. 9 that for $\alpha_N = 1$ the values Σq_N and $\Sigma q_C > 0$. Therefore, cations of dyes with rings of average polarity must undergo predominantly nucleophilic solvation.[21,22] Since Σq_N and Σq_C are the most similar for $\alpha = 1$ (see Fig. 9), it would be expected that nucleophilic solvation of the positively charged centers of the heterocycle and of the polymethine chain is approximately equal for these dyes.

Increasing α_N, starting from a unity, results in the shift of the positive charge from the terminal groups to the even positions of the polymethine chain. It can be seen from the values of Σq_N, Σq_C, and Σq^+_C that the positive charge is predominantly localized on the polymethine chain for all PD with weak electron-donor groups (see Fig. 9). Therefore, for this type of dye, nucleophilic solvation must occur mainly through the positively charged centers of the polymethine chain. The values of Σq^+_C and Σq_C increase as n increases. Therefore, increasing the length of the polymethine chain and decreasing the electron-donor ability of the terminal groups of PD with weak electron-donor rings should result in the enhancement of nucleophilic solvation and, hence, in broadening of the absorption bands, which is observed (see Fig. 4).

For dyes with strong electron-donor groups, the positive charge is predominantly shifted to the latter, and therefore the atoms of the heterocycle must undergo nucleophilic solvation first of all. The shift of the positive charge to the terminal groups increases as the electron-donor ability increases. In the case of the maximum electron-donor ability ($\alpha_N = 0$), the positive charge is completely localized at the heterocycles and the negative charge is localized on the chain. The values of Σq_N and Σq^+_C increase as n increases when α_N decreases from 1 to 0 (see Fig. 9). However, Σq_C decreases due to the increase in the negative charge at the odd positions of the chain. Starting from $\alpha_N = 0.5$ (very strong electron-donor ability), the localization of the negative charge is so significant that the net charge on the polymethine chain becomes negative and rapidly increases as the polymethine chain lengthens. It thus follows that for the dyes studied the broadening of the absorption bands when n and the electron-donor ability of the terminal groups increase may be due to the enhancement of both the nucleophilic solvation of the positively charged centers of the heterocycles and the electrophilic solvation of the negatively charged polymethine chain units by the solvent molecules.[22]

If electrophilic solvation plays a major role, the replacement of DMF by the significantly more electrophilic ethanol[22] should result in broadening of the bands for dyes **6—13**. However, as has been noted, the opposite situation is observed in our case. Therefore, for the higher vinylogs of symmetrical PD with strong electron-donor rings, like for compounds with weak electron-donor groups, the broadening of bands as the polymethine chain lengthens is caused by the enhancement of nucleophilic solvation. The difference is that for the latter this mainly occurs due to the localization of the positive charge on the chain, and for the former the localization is on the rings.

There is no such predominant localization of the positive charge for dyes with heterocyclic rings of moderate electron-donating ability (see Fig. 9). Therefore, nucleophilic solvation in them must be minimal. In fact, narrowing of the absorption bands in dichloromethane occurs up to tricarbocyanine for compounds **1—5** and **14—16**, whose rings possess more or less moderate electron-donor ability, whereas it is observed for dyes **17—30** and **6—13** whose rings are better and worse electron-donors, respectively, only when n increases from 0 to 1 for the former and from 1 to 2 for thiacyanines.

The influence of the length of the polymethine chain on fluorescence spectra of symmetrical PD

Lengthening the polymethine chain in dyes **1—24** results in a bathochromic shift of λ^f_{max}, like λ^a_{max}, by approximately 100 nm. As in the absorption spectra, the value of the vinylene shift is almost independent of the solvent. The values of these shifts calculated from λ_e also depend slightly on the nature of the solvent, and are in the range 100—130 nm (Fig. 10). It is significant that similar effects accompanying the increase in n, are also characteristic of the average positions of the fluorescent bands (see Fig. 3). Thus the change in M^{-1}_f differs from the changes in the average positions of the absorption bands, whose bathochromic shifts tend to decrease as the polymethine chain lengthens, especially in strongly nucleophilic solvents. The long-wave end descends smoothly in the fluorescent spectra and, on the contrary, the short-wave end descends in the absorption spectra. Therefore, the values of M^{-1}_f are bathochromically shifted relative to the band maximum, and M^{-1}_a are shifted hypsochromically. Dyes **1—24** possess fluorescent bands with vibrational maxima at the long-wave end. This shape is typical of symmetrical PD and is retained as n increases and the solvent changes (see Fig. 2, *b*). Therefore, the average positions of the fluorescent bands are shifted relative to λ^f_{max} by an almost constant value (20—40 nm depending on the irradiation range). As a consequence, the vinylene shifts calculated from the values of M^{-1}_{f} are constant. On the other hand, the shape of the absorption bands for PD **1—24** changes significantly as the polymethine chain lengthens, especially for strongly nucleophilic solvents (see Fig. 2, *a*). These changes are characterized by increasing intensities at the short-wave end of the band, which results in hypsochromic shifts of M^{-1}_{a} relative to $\lambda^{\mathrm{a}}_{\mathrm{max}}$. Therefore, in symmetrical PD the vinylene shifts of the average positions of the absorption bands tend to decrease as *n* increases and the nucleophilicity of the medium increases, unlike the analogous characteristics of fluorescent bands.

Regardless of the electron-donor ability of the heterocycles, lengthening the polymethine chain in **1—24** results in a decrease in ΔS_λ (Fig. 11). This can be interpreted in the following way. The positions of the maxima of the bands of symmetrical cyanines is determined by the distribution of the intensities of the vibronic transitions. In turn, this distribution depends on the degree of the change in the inter-ring equilibrium distances during excitation. Increasing *n* results in a regular decrease in this value. This results in an increase in the intensity of the purely electronic transition and a decrease in the intensity of the vibronic transitions. As a result, $\lambda^{\mathrm{a}}_{\mathrm{max}}$ and $\lambda^{\mathrm{f}}_{\mathrm{max}}$ shift to λ_{00}, which causes a decrease in the Stokes shift as the polymethine chain lengthens. Sometimes the accuracy of its determination noticeably decreases due to blurring of the band maximum (this can occur due to overlapping of vibronic interactions with similar intensities or due to the solvent effect). As a result, some ΔS_λ values may change irregularly with the change in chain length, as takes place on going from **1** to **2** and from **7** to **8** in DMF (see Fig. 11, *b*).

The value of ΔS_M changes less regularly with increasing *n* than ΔS_λ and, as a rule, decreases for the lower vinylogs and increases for the higher ones (see Fig. 11). M^{-1}_{a} and M^{-1}_{f} averaged over all vibronic transitions shift batho- and hypsochromically, respectively, *i.e.*, towards each other, in the same way as $\lambda^{\mathrm{a}}_{\mathrm{max}}$ and $\lambda^{\mathrm{f}}_{\mathrm{max}}$, due to the increase in the intensity of the 0—0 transition and shortening of the electron-vibration progression as

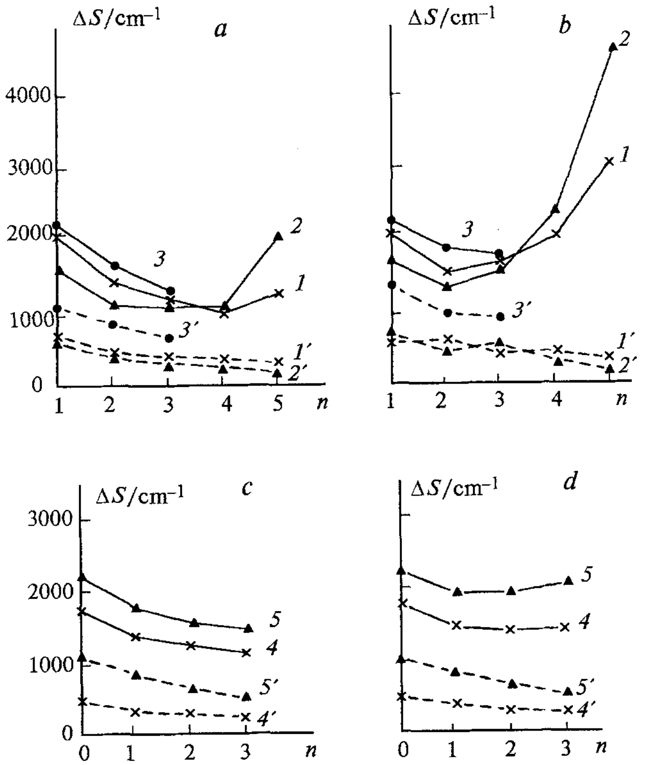


Fig. 10. Dependence of the Stokes shift calculated from the maxima (*1—5*) and the average positions of bands (*1′—5′*) for PD **1—13**, **17—24**, and **28—30** on the polymethine chain length. Designations for dyes and solvents are the same as in Fig. 2.

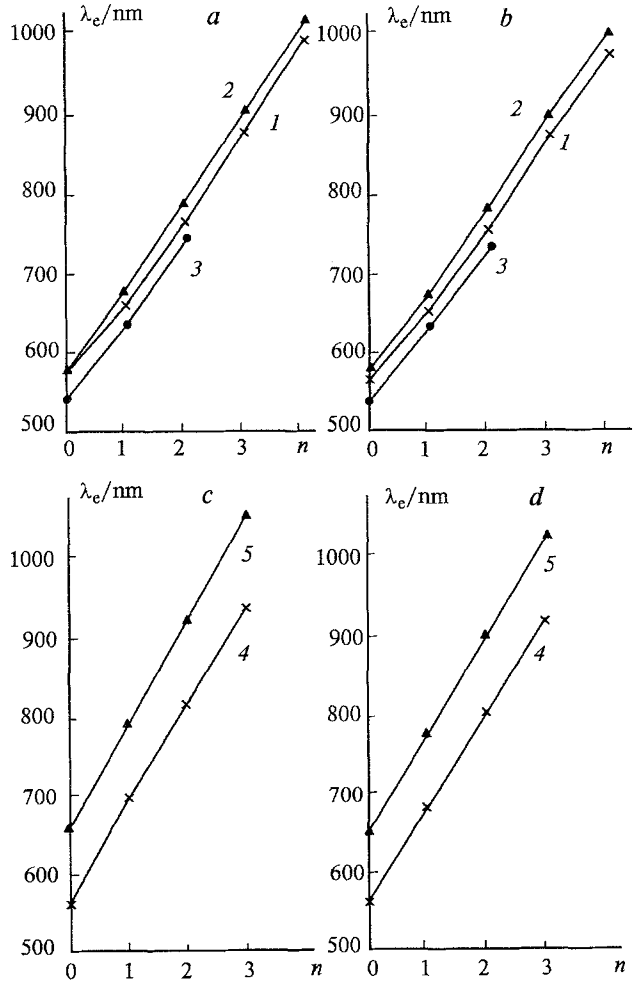


Fig. 11. Dependence of the wavelength at the intersection point of the long-wave absorption and fluorescent bands (*1—5*) for PD **1—13**, **17—24**, and **28—30** on the polymethine chain length. Designations for dyes and solvents are the same as in Fig. 2.

the polymethine chain lengthens. This shift of the average positions causes a decrease in ΔS_M. However, the significant increase in the intensities at the short-wave end of the absorption spectra under the action of a solvent (see Fig. 2, *a*) results in the hypsochromic shift of $M^{-1}{}_{a}$. The value of ΔS_M increases as n increases in the cases when this effect predominates (it usually predominates for higher vinylogs).

The luminescent ability of symmetrical cyanines at first glance changes rather chaotically as the polymethine chain lengthens. It can be unambiguously stated that only the transition from mono- to trimethinecyanines is accompanied by an increase in the fluorescence quantum yield (Fig. 12, ϕ values for indo- and thiamonomethinecyanines have been presented previously[23]). The small values of ϕ for PD with $n = 0$ may be explained by the arrangement of the nearby rings, which result in either a disturbance of the coplanarity[14] or the interaction of nonbonded heteroatoms.[15]

A further increase in n ambiguously affects the change in fluorescence quantum yields for dyes with different structures. For example, the luminescent ability of indo- and benzimidazolocyanines increases up to tri- and that of their thia-analogs increases up to dicarbocyanines (see Fig. 12). At the same time, the increase in n from 1 to 2 and further lengthening of the polymethine chain results in a decrease in ϕ for the dyes that are derivatives of benzo[*c*,*d*]indolium, pyrilium, and thiopyrilium (see Fig. 12).

These data show that the conclusion[23,24] that the fluorescence quantum yield is maximum for di- and tricarbocyanines for symmetrical PD is not always true. The fluorescent quantum yield may be maximum for carbocyanines as well (for example, **14**, **18**, and **22**). Since the PD studied differ significantly in the structure of their heterocycles, the conclusion can be drawn that the nature of the latter decisively affects the positions of the extrema of the ϕ dependence on n. These positions are not associated with the difference in the electron-donor ability of heterocycles, because the change in ϕ as the polymethine chain lengthens is inconsistent with the change in Φ_0. For example, despite the fact that the rings of indolium and benzo[*c*,*d*]indolium are similar in electron-donor ability, the fluorescence quantum yields change in opposite directions as n increases for the series of dyes **1—3** and **14—16**, and their absolute values sharply differ for the same n.

It can be proposed that the decrease in the luminescent ability of symmetrical cyanines with the increase in n is caused by the enhancement of isomerization processes in the excited state due to the increase in the number of bonds in the polymethine chain around which rotations are possible.[25] However, the processes mentioned should not significantly change for PD with $n > 2$ as the nature of rings changes, because the heterocycles are too far from one another to noticeably affect isomerization, as in the case of mono- and, sometimes, trimethinecyanines.[14] For a stronger proof of this supposition for compounds **15** and **16**, and **23** and **24** containing heterocycles with moderate and weak electron-donor ability, respectively, the values of ϕ were determined in a polymeric matrix in which isomerization of cyanines is essentially prevented. The fluorescence quantum yields in the matrix for the series of dyes presented above have the following values: 0.7 and 0.05 %; 1.5 and 0.5 %. Comparing these with the ϕ values in liquid solutions shows the luminescent ability of **15** and **16**, and **23** and **24** is significantly enhanced in the polymer. This testifies that isomerization processes considerably affect the absolute values of the fluorescent quantum yields. However, they do not play a determining role in the change in ϕ as the polymethine chain lengthens in symmetrical PD, because the tendencies in their changes as n increases are the same for liquid solutions and the matrix. They are also the same for solvents with different nucleophilicities: dichloromethane, ethanol, and DMF (see Fig. 12). Therefore, the changes in luminescent ability as the polymethine chain lengthens in cyanines, depending on the nature of the rings, is not associated with the difference in the degree of IMI in the dye—solvent system.

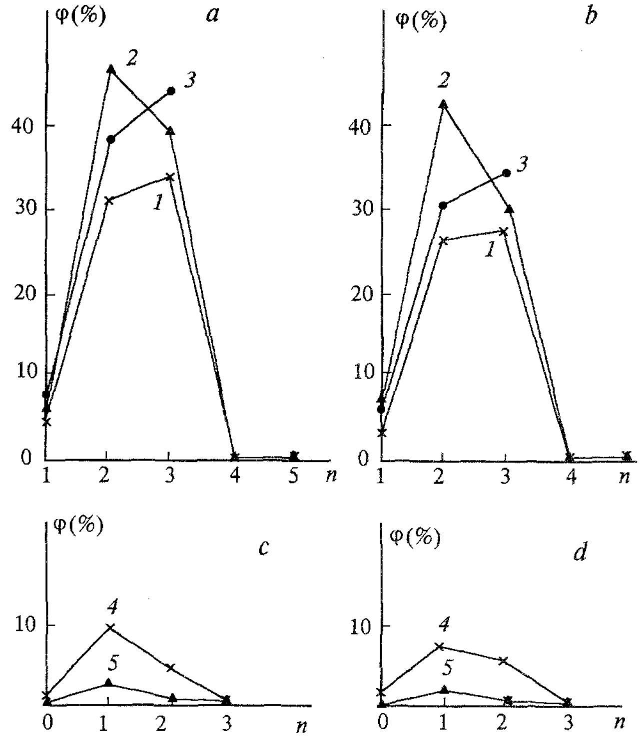


Fig. 12. Dependence of the fluorescence quantum yield (*1—5*) for PD **1—13**, **17—24**, and **28—30** on the polymethine chain length. Designations for dyes and solvents are the same as in Fig. 2.

The change in the value of ϕ as the polymethine chain lengthens may be caused by intersystem conversion, the probability of which depends on the structure of the heterocycles.[26] For example, it is 2.7 times higher for thiacyanines than for indocyanines. Hence, if the $S_1 \rightarrow T$ conversion played a determining role in the change in the fluorescence quantum yield as n increases in symmetrical PD, the values of ϕ for cyanines **6—10** would be significantly lower and would decrease considerably more rapidly than for compounds **1—5**. The opposite situation is observed in fact (see Fig. 12). The fact that intersystem conversion is not a major reason for the change in the fluorescent quantum yield as the polymethine chain lengthens agrees well with the high generation efficiency[23] of tetracarbocyanines **4** and **9**. This fact is very significant because the transition from tricarbocyanines **3** and **8** to the corresponding tetracarbocyanines is accompanied by a drop in ϕ by two orders of magnitude and the efficiency of generation[23] decreases by only 6—7 %. According to Fermi's golden rule, the probability of internal conversion increases[27] as the energy gap between the S_0 and S_1 states decreases and the vibronic interactions increase. The latter decrease regularly as the polymethine chain lengthens, as was mentioned in Ref. 27, and may cause only an increase in ϕ. Therefore, the decrease in the fluorescent quantum yields of symmetrical PD as n increases is mainly caused by the decrease in the energy gap between the ground and first excited states. It can be seen from the comparison of $\lambda^a{}_{max}$ and the values of ϕ that the 700 to 750 nm gap between the S_0 and S_1 states is the critical value of this interval at which the efficient influence of internal conversion on the luminescent ability of PD begins (see Figs. 2 and 12). Indeed, the transition from dicarbocyanines **2** ($\Delta\lambda^a{}_{max}$ = 640 to 652 nm) and **12** ($\Delta\lambda^a{}_{max}$ = 616 to 625 nm) to the corresponding tricarbocyanines **3** ($\Delta\lambda^a{}_{max}$ = 742 to 758 nm) and **13** ($\Delta\lambda^a{}_{max}$ = 715 to 730 nm) results in a sharp retardation in the increase in ϕ, and the similar transition from **7** ($\Delta\lambda^a{}_{max}$ = 658 to 665 nm) to **8** ($\Delta\lambda^a{}_{max}$ = 765 to 770 nm) is accompanied by a decrease in this value. The fluorescent quantum yield is rather small for carbocyanines **14** ($\Delta\lambda^a{}_{max}$ = 760 to 769 nm) and **22** ($\Delta\lambda^a{}_{max}$ = 750 to 762 nm) (see Fig. 12).

For an energy interval greater than 800 nm, internal conversion plays a dominant role in the deactivation of electron-excited states as the polymethine chain lengthens in symmetrical PD, regardless of the structure of their heterocycles or the value of n. Tetracarbocyanine **9** and dicarbocyanines **15**, **23**, which absorb in the same range (see Fig. 2), have rather low and almost equal values of ϕ (see Fig. 12).

Thus, the rate of decrease of the fluorescent quantum yield as the polymethine chain lengthens increases as the color of PD becomes deeper. The longer the effective length L of the heterocycles, the greater the deepening of the color. In our case, the L value is maximum for benzo[*c,d*]indolium and thiopyrilium. It is somewhat smaller for pyrilium rings. Therefore, the decrease in ϕ already occurs as n increases from 1 to 2 for PD **17—24**, whereas it begins at a longer chain length for PD **1—13**, which are based on rings with a small effective length.

As n increases unexpected changes are observed in the shapes of the fluorescent bands compared with those of the absorption bands for compounds **1—24** (see Fig. 4). It has been traditionally considered that the luminescent spectra must be mirror-symmetrical to the absorption spectra for organic dyes,[9] including PD. It thus should be expected that the tendencies in the changes in shapes of the fluorescent and absorption bands would be the same as n increases. What actually happens is that there are essential differences in their changes (see Fig. 2, *a*, *b*, 4, 6—8).

Any increase in n, regardless of the electron-donor ability of the heterocycles, causes narrowing of the fluorescent bands, unlike absorption bands for PD **1—24** (see Fig. 4). This occurs both in weakly and strongly nucleophilic solvents. Its value is somewhat lower for the latter than for the former.

The narrowing of the fluorescent bands as the polymethine chain lengthens testifies that the change in δ^f, unlike δ^a, is predominantly determined by vibronic interactions and not IMI. This conclusion agrees well with the fact that the narrowing of the fluorescent bands for any polymethine chain elongation is accompanied only by an increase in $\gamma^f{}_1$ (absolute value), $\gamma^f{}_2$, and F^f (see Figs. 6—8), regardless of the solvent. The dependences of these coefficients on n always have extrema for absorption spectra of **1—24** (see Figs. 6—8).

The described dependence of the shape of the fluorescent bands on the length of the polymethine chain indicates that IMI with a solvent for symmetrical PD are significantly weaker in the excited state than in the ground state.

It can be seen from Fig. 9 that the charge on a cation of a dye in the S_1 state, like in the S_0 state, is nonuniformly distributed depending on α_N and n. However, the distributions are considerably different for these states (see Fig. 9). For $\alpha_N = 0.5$ the positive charge in the S_1 state is shifted from the polymethine chain to the terminal groups to a greater extent than in the S_0 state. However, an increase in n results in changes in Σ^*q_N, Σ^*q_C and Σq_N, Σq_C in the opposite directions: Σ^*q_N, Σq_C decrease and Σq_N and Σ^*q_C increase. As a result, the uniformity of the charge distribution increases for the excited state and decreases for the ground state.

For $\alpha_N = 1$, Σ^*q_N and Σ^*q_C change as n increases in the same way as for $\alpha_N = 0.5$. However, their absolute values differ in the former case significantly less than in the latter case (see Fig. 9). Therefore, for PD with moderate electron-donor groups, greater conjugation of charge is achieved in the excited state as the polymethine chain lengthens than for cyanines with strongly electron-donor residues. It should be mentioned that in the ground state for $\alpha_N = 1$, conjugation also takes place as n increases due to the increase in Σq_N and the decrease in Σq_C. However, these values do not change as sharply as Σ^*q_N and Σ^*q_C. Therefore, for PD with moderate electron-donor heterocycles, as the polymethine chain lengthens, the charges on the excited state are conjugated to a greater extent than those in the ground state.

For $\alpha_N = 2$, an increase in n enhances the nonuniformity of the charge distribution for both of the states due to the decrease in Σq_N and $\Sigma^* q_N$ and the increase in Σq_C and $\Sigma^* q_C$ (see Fig. 9). Since the differences between $\Sigma^* q_N$ and $\Sigma^* q_C$ are less than those between Σq_N and Σq_C, greater charge compensation in the excited state than in the ground state is retained at rather high n for PD with weakly electron-donor residues.

Therefore, excitement of PD with various Φ_0 (45°, <45°, >45°) results in a large redistribution of charge. Even the sign at many atoms changes to the opposite.[11] As a result, the molecule of a dye must either rearrange its solvate shell or lose it before irradiation. In any case, an essential weakening of the specific Coulomb interactions occurs in the excited state, because they are mainly caused by the nucleophilic solvation of the positively charged centers of the cation by the dipoles of the solvent molecule.[14] The values of the charges of these very centers in the S_1 state decrease to the greatest extent, which can be seen especially distinctly by comparing the values of the net positive charges in the excited and ground states $[(\Sigma^* q_N + \Sigma^* q^+_C) < (\Sigma q_N + \Sigma q^+_C)]$ (see Fig. 9).

* * *

The results of the studies of the dependence of the spectral-luminescent properties of symmetrical PD on the length of the polymethine chain may be generalized as follows.

1. For various types of symmetrical PD, elongation of the polymethine chain results in a bathochromic shift of $\lambda^a{}_{max}$, λ_e, $\lambda^f{}_{max}$, and $M^{-1}{}_f$ by approximately 100—130 nm. These values weakly depend on the electron-donor ability of the heterocycles and the nature of the solvent. The vinylene shifts of the average positions of the absorption bands, on the other hand, depend significantly on these factors. There is a tendency for these shifts to decrease as n increases when Φ_0 deviates to either sides of 45° and when the nucleophilicity of the solvent increases.

2. Lengthening the polymethine chain of symmetrical PD causes a decrease in the Stokes shift, which is caused by the weakening of the vibronic interactions.

3. At first the fluorescent quantum yield increases as the chain lengthens and then decreases as it lengthens further. The greater the effective length of the heterocycles the sooner the decrease begins. The decrease in ϕ is mainly caused by the increase in internal conversion due to the decrease in the energy gap between the S_0 and S_1 states as n and L increase.

4. The change in the shapes of absorption bands as the polymethine chain lengthens is caused by the competitive influence of vibronic interactions and IMI for cationic symmetrical dyes. The former decay as n increases and cause narrowing of the bands, and an increase in their asymmetry, steepness, and structuring (increase in $\gamma^a{}_1$, $\gamma^a{}_2$, and $F^{\,a}$, respectively) for the lower vinylogs. On the other hand, IMI are enhanced as the polymethine chain lengthens. As a result, the band narrowing decreases with the initial increase in n (or does not occur at all) and with further lengthening of the polymethine chain the bands broaden and their $\gamma^a{}_1$, $\gamma^a{}_2$, and $F^{\,a}$ values decrease. The greater the nucleophilicity of the solvent and the stronger the deviation of the electron-donor ability of the terminal heterocyclic groups of the dyes from average, the sooner these changes begin.

Unlike the absorption spectra of symmetrical PD, in their fluorescent spectra any elongation of the polymethine chain, regardless of the electron-donor ability of the heterocycles or the solvent, results in narrowing of the bands and an increase in $\gamma^a{}_1$, $\gamma^a{}_2$, and $F^{\,a}$. This is caused by the fact that vibronic interactions, and not IMI as in absorption, play a predominant role in changing the shape of the luminescent bands as n increases.

References

1. A. A. Ishchenko, *Usp. Khim.*, 1991, **60**, 1708 [*Russ. Chem. Rev.*, 1991, **60** (Engl. Transl.)].
2. N. Tyutyulkov, J. Fabian, A. Mehlhorn, F. Dietz, and A. Tadjer, *Polymethine Dyes. Structure and Properties.* St. Kliment Ohridski University Press, Sofia, 1991, 249.
3. *Infrared Absorbing Dyes*, Ed. M. Matsuoka, Plenum Press, New York—London, 1990, 220.
4. T. H. James, *The Theory of the Photographic Process*, McMillan Publishing, New York, 1977.
5. N. P. Vasilenko and F. A. Mikhailenko, *Ukr. Khim. Zh.* [*Ukr. Chem. J.*], 1986, **52**, 401 (in Russian).
6. A. I. Tolmachev, M. A. Kudinova, and N. A. Derevyanko, *Khim. Geterotsikl. Soedin.*, 1974, 53 [*Chem. Heterocycl. Compd.*, 1974 (Engl. Transl.)].
7. A. I. Tolmachev, N. A. Derevyanko, and M. A. Kudinova, *Khim. Geterotsikl. Soedin.*, 1975, 617 [*Chem. Heterocycl. Compd.*, 1975 (Engl. Transl.)].
8. G. G. Dyadyusha and A. A. Ishchenko, *Zh. Prikl. Spektr.* [*J. Appl. Spectr.*], 1979, **30**, 1037 (in Russian).
9. V. I. Permogorov, L. A. Serdyukova, and M. D. Frank-Kamenetskii, *Optika i Spektroskopiya* [*Optics and Spectroscopy*], 1968, **25**, 77 (in Russian).
10. A. A. Ishchenko, V. A. Svidro, N. A. Derevyanko, Yu. L. Slominskii, and A. I. Tolmachev, *Optika i Spektroskopiya* [*Optics and Spectroscopy*], 1989, **66**, 1302 (in Russian).
11. A. A. Ishchenko, V. A. Svidro, and N. A. Derevyanko, *Dyes and Pigments*, 1989, **10**, 85.
12. S. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam—London—New York, 1968.
13. S. F. Meison, *Khimiya sinteticheskikh krasitelei* [*Chemistry of Synthetic Dyes*], Ed. K. Venkataraman, Khimiya, Leningrad, 1974, **3**, 1817 (Russ. Transl.).
14. A. M. Kolesnikov and F. A. Mikhailenko, *Usp. Khim.*, 1987, **56**, 466 [*Russ. Chem. Rev.*, 1987, **56** (Engl. Transl.)].

15. S. V. Sereda, A. A. Ishchenko, M. A. Kudinova, V. V. Kurdyukov, and A. I. Tolmachev, *Zh. Strukt. Khim.*, 1992, **33**, 139 [*J. Struct. Chem.*, 1992, **33** (Engl. Transl.)].
16. 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.)].
17. A. A. Ishchenko, *Ukr. Khim. Zh.* [*Ukr. Chem. J.*], 1991, **57**, 1166 (in Russian).
18. S. Dhne, *Science*, 1978, **199**, 1163.
19. T. Tani, *J. Photogr. Sci.*, 1971, **19**, 161.
20. S. Dhne and S. Kulpe, *Abh. Akad. Wiss. DDR, Abt. Math., Naturwiss., Techn.*, 1977, No. 8, 1.
21. N. A. Derevyanko, G. G. Dyadyusha, A. A. Ishchenko, and A. I. Tolmachev, *Teor. Eksp. Khim.*, 1983, **19**, 169 [*Theor. Exp. Chem.*, 1983, **19** (Engl. Transl.)].
22. V. A. Palm, *Osnovy kolichestvennoi teorii organicheskikh reaktsii* [*Foundations of the Theory of Organic Reactions*], Khimiya, Leningrad, 1977, 359 (in Russian).
23. V. A. Mostovnikov, A. N. Rubinov, M. A. Al'perovich, V. I. Avdeeva, I. I. Levkoev, and M. M. Loiko, *Zh. Prikl. Spektr.* [*J. Appl.. Spectr.*], 1974, **20**, 42 (in Russian).
24. L. J. E. Hofer, R. J. Grabenstetter, and E. O. Wiig, *J. Am. Chem. Soc.*, 1950, **72**, 203.
25. V. A. Kuz'min, *Usp. Nauch. Fotogr.* [*Adv. Scient. Photogr.*], 1984, **22**, 90 (in Russian).
26. K. M. Romanek and O. Hildebrand, *Laser Focus*, 1977, **13**, 50.
27. J. Barltrop and J. Coil, *Vozbuzhdennye sostoyaniya v organicheskoi khimii* [*Excited States in Organic Chemistry*], Mir, Moscow, 1978, 447 (Russ. Transl.).

Received November 29, 1993