Dyes and Pigments **19** (1992) 169–177

Constitution and Fluorescence Spectra of Unsymmetrical Polymethine Dyes

A. A. Ishchenko, N. A. Derevyanko & V. A. Svidro

Institute of Organic Chemistry, Academy of Sciences of Ukraine,
Murmanskaya, 5, Kiev-94, 253660, Ukraine

(Received 30 January 1992; accepted 10 March 1992)

ABSTRACT

The regularities in the fluorescence spectra of typical electron-unsymmetrical polymethine dyes were found to be similar to those of the corresponding symmetrical dyes, in contrast to absorption spectra. The fluorescence spectra exhibit constant vinylene shifts (c. 100 nm) for a widely varied degree of electronic asymmetry, band maxima almost free of deviations, and band shapes characteristic of most organic dyes which are slightly affected by the nature of a solvent. In contrast, in the absorption spectra, increase in electronic asymmetry is accompanied by decreasing vinylene shifts, increasing deviations, notably changing band shapes and increasing solvatochromic effects. Based on quantum-chemical calculations, the atomic charges and bond orders of unsymmetrical dyes were shown to be considerably more equalized in the excited than in the ground state, which causes the essential difference between their fluorescence and absorption spectra.

1 INTRODUCTION

Unsymmetrical polymethine (cyanine) dyes (PD) differ from the corresponding symmetrical (parent) ones in some absorption spectral features.[1–3] Thus, vinylene shifts diminish with lengthening of the polymethine chain,[1] band shapes diverge from the standard contour typical of many organic dye classes,[4] and very large solvatochromic effects are apparent.[1,5] These factors distinguish unsymmetrical PD from symmetrical dyes. The former are also

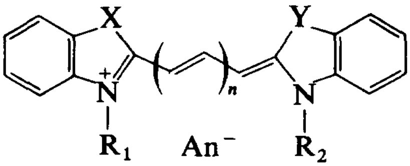
Dyes and Pigments 0143-7208/92/$05.00

found to show hypsochromic shifts of absorption maximum, as compared with the arithmetical mean of the respective parent-dye maxima.[6] This shift, referred to as deviation, quantitatively characterizes the electronic asymmetry of cyanines.[6]

As was previously reported,[7,8] the fluorescence spectra of some unsymmetrical PDs exhibit some features which are different from those of absorption spectra. However, no relationships have been reported concerning the change of fluorescence within dye series, and this paper is the first in a systematic study of this problem.

2 MATERIALS AND METHODS

The dyes studied have the general formula



I–IX

I–III, $X = S$, $Y = C(Me)_2$, $R_1 = Et$, $R_2 = Me$; **IV–VI**, $X = NPh$, $Y = S$, $R_1 = Ph$, $R_2 = Et$; **VII–IX**, $X = NPh$, $Y = C(Me)_2$, $R_1 = Ph$, $R_2 = Me$; **I, IV, VII**, $n = 1$; **II, V, VIII**, $n = 2$; **III, VI, IX**, $n = 3$; **I, II, IV, V, VII**, An = I; **III, VI, VIII, IX**, $An = CO_4$.

The regularities in the absorption spectra and the preparation of dyes **I–IX** have been previously described.[1] The fluorescence spectra were measured on an SDL-1 (USSR) spectrofluorimeter in the same solvents as those used for absorption spectroscopic measurements, viz. methylene chloride (MC), ethanol and dimethyl formamide (DMF). The mathematical treatment of fluorescence spectra involved the method of moments.[9] The results are presented in Table 1, including mean positions M^{-1} which are the reciprocal of mean frequencies $\bar{\nu}$,[9] widths (σ), coefficients of asymmetry (γ_1), excess (γ_2) and fine structure of fluorescence bands (F) for dyes **I–IX**. Their maxima (λ_{max}), deviations (D_λ and D_M), Stokes shifts (ΔS_λ and ΔS_M) and fluorescence quantum yields (φ) are also shown. Values of D_λ and ΔS_λ were calculated through λ_{max}, whereas D_M and ΔS_M were calculated using M^{-1}. The values of φ were determined relative to the fluorescence quantum yield of the corresponding symmetric PD.[9,10]

Quantum-chemical calculations in the HMO-approximation were carried out using previously used parameters.[1] The electronic asymmetry was simulated[1] by varying the alternation amplitude for the resonance integrals

TABLE 1
Parameters of Fluorescence Bands for Dyes I–IX

Dye	*Solvent*	λ_{max} (*nm*)	D_λ (*nm*)	φ (*%*)	M^{-1} (*nm*)	D_M (*nm*)	σ (*cm*$^{-1}$)	γ_1	γ_2	*F*	ΔS_λ (*cm*$^{-1}$)	ΔS_M (*cm*$^{-1}$)
I	MC	572	3	5	590·8	4·5	960	−1·18	2·2	0·060	699	1 822
	Ethanol	573	−0·5	3	591·5	1	970	−1·16	2·2	0·059	863	2 048
	DMF	575	1·5	4	597·5	−1·1	977	−1·16	2·0	0·059	791	2 103
II	MC	674	3	35	706·9	−8·3	838	−1·40	3·1	0·080	407	1 523
	Ethanol	675	−2·5	30	694·6	−1·9	850	−1·37	2·9	0·078	570	1 626
	DMF	678	−1·5	29	696·7	−4	861	−1·35	2·8	0·077	588	1 637
III	MC	788	5	36	825·8	−13·7	752	−1·55	3·8	0·095	331	1 447
	Ethanol	791	−6	30	806·7	−1·1	784	−1·51	3·5	0·092	430	1 813
	DMF	793	−4	29	812·3	−1	803	−1·48	3·3	0·091	548	1 979
IV	MC	563	6	5	581·1	7·4	955	−1·01	1·9	0·038	1 106	2 299
	Ethanol	564	3·5	4	578·4	7·8	960	−0·99	1·8	0·035	1 281	2 427
	DMF	567	7·5	5	582·5	7·3	962	−1·02	2·0	0·035	1 302	2 510
V	MC	664	8·5	40	687·5	8·5	859	−1·14	2·7	0·057	914	2 180
	Ethanol	662	6·5	30	682·0	3·1	868	−1·11	2·5	0·056	1 023	2 498
	DMF	670	2·5	32	690·1	−0·9	873	−1·10	2·4	0·055	1 257	2 816
VI	MC	777	4·5	33	797·7	7·0	786	−1·22	3·2	0·072	1 019	2 488
	Ethanol	777	1	26	790·1	11·0	826	−1·18	3·0	0·070	1 518	3 054
	DMF	779	5	25	796·4	7·8	850	−1·15	2·6	0·068	2 667	3 479
VII	MC	554	10	5	580·9	3·6	1 010	−1·02	2·1	0·035	1 480	3 085
	Ethanol	553	9	3	574·3	7·4	1 027	−1·00	1·9	0·033	1 680	3 206
	DMF	558	7	3	579·2	5·5	1 040	−0·99	1·7	0·032	1 764	3 324
VIII	MC	659	7·5	28	689·6	−3·5	950	−1·08	2·4	0·045	1 492	3 055
	Ethanol	657	6	22	677·7	4·1	981	−1·05	2·2	0·042	2 020	3 423
	DMF	658	8	20	691·1	−4·2	1 002	−1·03	1·9	0·040	2 408	3 882
IX	MC	762	14·5	26	781·3	16·6	910	−1·12	2·6	0·051	1 983	3 119
	Ethanol	763	7·5	22	778·3	14·9	967	−1·08	2·3	0·046	3 154	4 024
	DMF	764	9	20	785·3	11·0	991	−1·06	2·2	0·043	3 522	4 357

β of the bonds in the polymethine chain (PC). Table 2 shows the total positive charges (Σq_1^+, Σq_2^+) and total charges (Σq_1, Σq_2) evaluated for ground and excited (*) states (subscripts 1 and 2 correspond to stronger and weaker electron-donor nuclei, respectively, i.e. benzimidazolium and benzthiazolium[1]), and the values of the bond alternation parameter (ΔP) are as described previously.[11]

3 RESULTS AND DISCUSSION

Table 1 shows that the lengthening of PC in compounds **I**–**III** exhibiting slight electronic asymmetry causes a regular bathochromic shift of λ_{max} by

TABLE 2

Quantum-Chemical Data for Dyes **IV–VI** with the Various Alternation Amplitudes of β in Polymethine Chain

β_{C-C}	$\beta_{C=C}$	n	Σq_1^+	Σq_1	Σq_2^+	Σq_2	ΔP	$\Sigma^* q_1^+$	$\Sigma^* q_1$	$\Sigma^* q_2^+$	$\Sigma^* q_2$	ΔP^*
1·00	1·00	1	0·8767	0·7257	0·6744	0·5272	0·1077	0·8021	0·6297	0·6199	0·4870	0·1015
		2	0·8820	0·7330	0·6830	0·5390	0·1027	0·8360	0·6800	0·6350	0·5133	0·0971
		3	0·8862	0·7386	0·6893	0·5475	0·0981	0·8559	0·7059	0·6560	0·5308	0·0929
0·98	1·02	1	0·8939	0·7463	0·6532	0·5024	0·1093	0·7898	0·6098	0·6310	0·5101	0·1014
		2	0·9032	0·7588	0·6559	0·5072	0·1045	0·8256	0·6638	0·6504	0·5346	0·0969
		3	0·9103	0·7681	0·6576	0·5100	0·1000	0·8481	0·6935	0·6692	0·5493	0·0927
0·96	1·04	1	0·9102	0·7660	0·6326	0·4783	0·1110	0·7771	0·5891	0·6429	0·5332	0·1012
		2	0·9228	0·7827	0·6300	0·4768	0·1075	0·8151	0·6473	0·6661	0·5565	0·0967
		3	0·9325	0·7951	0·6280	0·4749	0·1052	0·8403	0·6811	0·6827	0·5685	0·0928
0·94	1·06	1	0·9261	0·7851	0·6128	0·4550	0·1142	0·7642	0·5682	0·6566	0·5569	0·1010
		2	0·9414	0·8050	0·6058	0·4481	0·1130	0·8042	0·6300	0·6819	0·5788	0·0964
		3	0·9521	0·8189	0·6008	0·4429	0·1126	0·8323	0·6681	0·6965	0·5885	0·0930
0·92	1·08	1	0·9407	0·8027	0·5937	0·4329	0·1174	0·7513	0·5467	0·6745	0·5804	0·1014
		2	0·9581	0·8251	0·5831	0·4216	0·1182	0·7931	0·6125	0·6978	0·6014	0·0975
		3	0·9695	0·8397	0·5761	0·4138	0·1196	0·8237	0·6547	0·7107	0·6092	0·0948
0·90	1·10	1	0·9548	0·8196	0·5757	0·4117	0·1206	0·7380	0·5246	0·6922	0·6039	0·1026
		2	0·9736	0·8438	0·5622	0·3969	0·1232	0·7812	0·5936	0·7139	0·6245	0·0997
		3	0·9849	0·8583	0·5540	0·3877	0·1262	0·8145	0·6401	0·7256	0·6309	0·0983
0·88	1·12	1	1·0207	0·8979	0·4872	0·3086	0·1392	0·6676	0·3846	0·8065	0·7420	0·1146
		2	1·0369	0·9183	0·4710	0·2899	0·1497	0·7020	0·4622	0·8236	0·7651	0·1183
		3	1·0432	0·9262	0·4648	0·2828	0·1583	0·7421	0·5231	0·8299	0·7729	0·1229
0·86	1·14	1	0·9801	0·8497	0·5422	0·3728	0·1266	0·7115	0·4793	0·7293	0·6511	0·1065
		2	0·9995	0·8745	0·5257	0·3541	0·1324	0·7566	0·5540	0·7484	0·6717	0·1057
		3	1·0098	0·8878	0·5169	0·3440	0·1379	0·7944	0·6080	0·7563	0·6769	0·1063
0·84	1·16	1	0·9915	0·8633	0·5271	0·3551	0·1294	0·6981	0·4559	0·7492	0·6745	0·1085
		2	1·0106	0·8876	0·5099	0·3356	0·1366	0·7435	0·5327	0·7656	0·6952	0·1088
		3	1·0199	0·8993	0·5015	0·3259	0·1431	0·7827	0·5893	0·7735	0·7007	0·1104
0·78	1·22	1	0·9678	0·8352	0·5584	0·3916	0·1236	0·7247	0·5021	0·7101	0·6276	0·1045
		2	0·9871	0·8597	0·5432	0·3742	0·1279	0·7692	0·5744	0·7308	0·6479	0·1027
		3	0·9981	0·8739	0·5343	0·3644	0·1322	0·8046	0·6244	0·7407	0·6535	0·1023

c. 100–110 nm, a value similar to that for the corresponding symmetric PD.[9,10] It is of interest to note that, in contrast to the vinylene shift in the absorption spectra, the shift in the fluorescence spectra remains almost constant on progressing to much more electron-unsymmetrical PD (**IV**–**IX**) and it does not decrease with increase in the nucleophilic properties of the solvent. Thus, the second vinylene shift observed in DMF (106 nm) for (benzimida)(indo)cyanines (**VIII**, **IX**), compounds characterized by the most pronounced electron asymmetry, is very similar to that in MC (103 nm), and

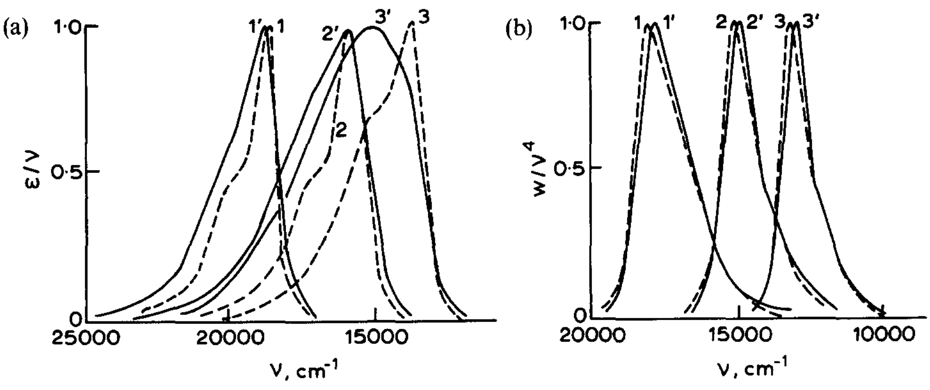


Fig. 1. Absorption (a) and fluorescence (b) spectra of dyes **IV–VI** in MC (curves 1, 2, 3) and DMF (1', 2', 3').

it is practically equal to the first (102 and 103 nm in MC and DMF, respectively) and second (114 and 115 nm in MC and DMF, respectively) vinylene shifts of (thia)(indo)cyanines (**I–III**), which can be regarded as electron-unsymmetrical PD to only a very slight degree (see Table 1). In comparison with the absorption spectra, an increase in the electron asymmetry results in the absorption vinylene shifts decreasing to 34 nm in DMF and to 62 nm in MC.[1] A factor accentuating the contrast of absorption and fluorescence vinylene shifts is that the latter do not practically attenuate even for the mean positions of the fluorescence bands. (Benzimida)(indo)cyanines serve as an example: the second vinylene shifts in their fluorescence spectra are 91·7 nm in MC and 94·2 nm in DMF, while in the absorption spectra the values decrease to 58·6 and 40·2 nm, respectively.[1] Such a striking difference arises from the fact that the fluorescence band shapes are much less influenced by the lengthening of the PC, as compared with the absorption spectra (see Fig. 1). Therefore, the points of M^{-1}, contrary to the analogous absorption parameter, are displayed by almost the same distances from the band maxima, leading to nearly constant vinylene shifts of the mean fluorescence band positions.

The deviations of band maxima are notably lower in fluorescence than in absorption spectra (see Table 1 and Ref. 1) with respect to both D_λ and D_M. For instance, PD **IX** (the most electron-unsymmetrical compound among the investigated dyes) is characterized by parameters D_λ and D_M being 9·0 and 11·0 nm for fluorescence and 128·5 and 113·4 nm for absorption.[1]

The Stokes shifts of the slightly electron-unsymmetrical dyes **I–III**, evaluated through their band maxima, are slightly different from those of symmetrical dyes.[9,10] With increase in *n*, both dye types show a decreasing value of ΔS_λ in all solvents. The same holds for ΔS_M in MC (see Table 1). In ethanol and DMF, which are more polar and nucleophilic than MC, these parameters increase on increasing n from 2 to 3.

The more electron-unsymmetrical PD **IV–VI** have values of ΔS_λ and ΔS_M essentially larger than those of the respective symmetrical dyes (see Table 1 and Refs 9 and 10). On going from carbo- to dicarbocyanines, the values of ΔS_λ decrease, but on further lengthening of the PC, with n increasing from 2 to 3, they increase, unlike the case of the parent cyanines. In MC, the parameter ΔS_M behaves similarly, and in ethanol or DMF it increases with lengthening of the PC.

When the electron asymmetry becomes even more pronounced (on going from PD **IV–VI** to **VII–IX**), the Stokes shifts of both band maxima and mean positions increase progressively (see Table 1). Lengthening the PC, as in the (benzimida)(indo)cyanines **VII–IX**, is accompanied only by increase in the values of ΔS_λ and ΔS_M.

The fluorescence quantum yields of PD **I–III** are much the same as those of the corresponding symmetrical PD. Compounds **VI**, **VIII** and **IX**, which are notably more unsymmetrical than PD **I–III**, are characterized by lower quantum yields compared to their parent PD, although they have the rather larger absolute values typical of cyanines with an open PC (see Table 1).

The fluorescence and absorption band shapes for PD **I–III** are similar, while for PD **IV–IX** they differ considerably (see Fig. 1). The fluorescence band shapes of unsymmetrical PD, irrespective of their degree of asymmetry, were found to be similar to those of symmetric PD (see Fig. 1 and Ref. 10), including the slight sensitivity to the nature of a solvent.

The fluorescence bands of PD **I–IX** are much narrower than the absorption bands, the differences decreasing with lengthening of the PC and increase in the difference in electron-donor ability of the end-groups (see Table 1 and Ref. 1).

Lengthening of the PC, as in slightly electron-unsymmetrical compounds **I–III**, results, as with the parent dyes,[9,10] in the fluorescence bands becoming narrower and the parameters γ_1, γ_2, F increasing in any solvent. The analogous tendency was also observed for the more unsymmetrical PD **IV–IX**. Nevertheless, the effect of PC lengthening weakens as the electron asymmetry increases in the dye series, such as (thia)(indo)-, (benzimida)(thia)- and (benzimida)(indo)cyanines. For PD **VII–IX** the changes in the parameters are quite negligible compared to the parent cyanines (see Table 1 and Ref. 10). It is noteworthy that for PD **IV–IX** increasing n causes the opposite effect on the band widths, and for PD **VII–IX** this concerns also the band asymmetry, excess and fine structure.

In order to interpret the luminescent properties of unsymmetrical PD, the electron distributions in the S_0 and S_1 states were compared; quantum-chemical calculations were carried out for PD **IV–VI**.

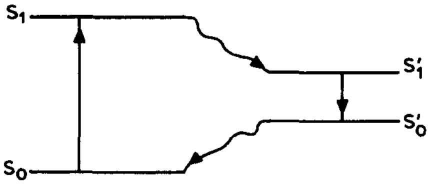


Fig. 2. Electron transitions in molecules of polymethine dyes occurring on absorption ($S_0 \rightarrow S_1$) and emission ($S_1' \rightarrow S_0'$) of light.

It is apparent from Table 2 that, on excitation, the values $\Sigma^* q_1^+$ and $\Sigma^* q_2^+$, $\Sigma^* q_1$ and $\Sigma^* q_2$ differ much less than the analogous parameters in the ground state, at all considered alternation amplitudes of β. For instance, taking the amplitude equal to 10% the authors obtained for PD **VI**: $\Sigma^* q_1^+ = 0{\cdot}8145$, $\Sigma^* q_2^+ = 0{\cdot}7256$, $\Sigma^* q_1 = 0{\cdot}6401$, $\Sigma^* q_2 = 0{\cdot}6309$, and $\Sigma q_1^+ = 0{\cdot}9849$, $\Sigma q_2^+ = 0{\cdot}5540$, $\Sigma q_1 = 0{\cdot}8583$, $\Sigma q_2 = 0{\cdot}3877$.

The notable equalization of charges within the heterocyclic residues, and hence of their electron-donor abilities, suppresses the bond order alternation in them to a great extent, which is apparent on comparing the values ΔP and ΔP^*: for PD **VI** these values are 0·1262 and 0·0983, respectively, at the same amplitude $\beta = \pm 10\%$.

Since the four-level scheme holds good for the electronic states of cyanines,[11] the geometry of the ground state is assumed to be retained by the molecule during light absorption (transition $S_0 \rightarrow S_1$), whereas emission (transition $S_1' \rightarrow S_0'$) occurs at the geometry of the excited state (Fig. 2). The charges and the bond orders in the stationary state S_1' should approximate to those of the non-stationary Franck–Condon state S_1, since the relaxation radiationless transition $S_1 \rightsquigarrow S_1'$ is mainly accompanied by adjustment of the nuclear configuration according to the change in electron distribution on excitation.[11] The bond orders in these states are essentially equalized relative to the ground state, and hence the vinylene shifts are much greater, and the deviations are much smaller for fluorescence than for absorption, with the unsymmetrical PD **I–IX**. The same reason accounts for the smaller change in the internuclear equilibrium distances and hence in vibronic interactions during the transition $S_1' \rightarrow S_0'$, compared to $S_0 \rightarrow S_1$. As a result, the fluorescence bands of the cyanines **I–IX** become narrower than the absorption bands and assume a shape resembling that of symmetrical PD.

For PD with a small alternation amplitude of β (i.e. the case of slight electron asymmetry), bond order alternation decreases in both excited and ground states, i.e. values ΔP^* and ΔP diminish. This weakens the vibronic interactions, resulting in narrowing of the fluorescence and absorption bands, increase in their asymmetry, excess and fine structure, with accompanying increase of n. As the electron asymmetry increases, the decrease in the values of ΔP^* and ΔP observed with lengthening of the PC diminishes, this dependence being rather non-uniform. Thus, at the β amplitude equal to $\pm 8\%$, the values ΔP^* continue to decrease, while ΔP increases (see Table 2). Therefore, the effects on fluorescence spectra of lengthening the PC, viz. band narrowing and increase in γ_1, γ_2, F, develop slower in the dye series **VII–IX** compared to the series **IV–VI**. The absorption spectra of dyes **IV–IX** demonstrate the band broadening which occurs on increasing n, and in the case of PD **VII–IX** this is also accompanied by a decrease in asymmetry, excess and fine structure of bands.

If the amplitude of β alternation exceeds 10% (the case of strong electron asymmetry), the bond alternation increases in the excited state, i.e. ΔP^* increases. However, this is not the case as far as unsymmetric PD **I–IX** are concerned, because increasing n causes, in fact, narrowing rather than broadening of the fluorescence bands for all these PD. It should be pointed out that the bond alternation, which is sufficiently pronounced to observe the fluorescence band broadening as n increases, is realized for pyridopyrylopolycarbocyanines, described recently as the most electron-unsymmetrical cyanines currently known.[2] Since the increase in ΔP demands less alternation of β than that in ΔP^*, the Stokes shifts and the values for PD **IV–IX** change oppositely with lengthening PC: the former values increase while the latter diminish, in contrast to their parent dyes and to the slightly electron-unsymmetrical PD **I–III**. The increase of ΔS_λ and ΔS_M with lengthening PC in PD **IV–IX** is caused by the large shifts in the absorption band maxima and the mean positions to the short-wavelength region. Hypsochromic shifts result from the increase in intensity of the short-wavelength vibronic transitions accompanied by attenuation of the O–O transition in the absorption spectra, which occurs on increasing bond alternation in the S_0 state (increase in ΔP) with lengthening PC. These processes become more probable in nucleophilic solvents.[1] That is why, when going from MC to ethanol or DMF, one observes the additional increase in the Stokes shifts for PD **I–IX**. Provided the electron asymmetry is so great that lengthening the PC makes ΔP^* increase as well as ΔP, the values ΔS_λ and ΔS_M also increase, due to the bathochromic shifts of the fluorescence band maxima and mean-positions (the long-wavelength vibronic transitions in fluorescence spectra should become more intense than O–O transitions).

The atomic charges, which are much more equalized and smaller in absolute value for the excited state than for the ground state, lead the former to provide the weaker nucleophilic solvation. This accounts for the additional narrowing of bands in the fluorescence spectra and the considerably smaller solvent effects compared to the absorption spectra.

Thus, the electronic excitation of unsymmetrical PD molecules leads to a substantial equalization of both atomic charges and bond orders. Therefore, the regularities of their fluorescence spectra, contrary to absorption spectra, resemble those of symmetrical cyanines.

REFERENCES

1. Ishchenko, A. A., Zubarovskii, V. M., Gromova, G. A. & Derevyanko, N. A., *Zh. Org. Khim.*, **23** (1987) 621.
2. Derevyanko, N. A., Ishchenko, A. A., Slominskii, Yu. L. & Tolmachev, A. I., *Mendeleev Commun.*, **3** (1991) 91.
3. Ishchenko, A. A., Derevyanko, N. A., Zubarovskii, V. M. & Tolmachev, A. I., *Theoret. Experim. Khim.*, **20** (1984) 443.
4. Ishchenko, A. A., *Usp. Khim.*, **60** (1991) 1708.
5. Vompe, A. F., Meskhi, L. M., Tyurin, V. S., Yagupol'skii, L. M. & Troitskaya, V. L., *Dokl. Akad. Nauk SSSR*, **272** (1983) 615.
6. James, T. H., *The Theory of the Photographic Process.* Macmillan Publishing Co., New York, 1977.
7. Bondar, M. V. *et al.*, *Kvantovaya Elektron.*, **11** (1984) 462.
8. Dyadyusha, G. G., Alperovich, M. A., Tyurin, V. S. & Kachkovskii, A. D., *Ukr. Khim. Zh.*, **51** (1985) 298.
9. Ishchenko, A. A., Svidro, V. A. & Derevyanko, N. A., *Dyes and Pigments*, **10** (1989) 85.
10. Ishchenko, A. A., Derevyanko, N. A. & Svidro, V. A., *Opt. Spectrosk.*, **72** (1992) 110.
11. Ishchenko, A. A., Svidro, V. A., Derevyanko, N. A., Slominskii, Yu. L. & Tolmachev, A. I., *Opt. Spectrosk.*, **66** (1989) 1302.