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The photophysical and photochemical properties of the oxacarbo-cyanine and thiacarbo-cyanine dyes

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Abstract

The photophysical and photochemical properties of the oxacarbo-cyanine and thiacarbo-cyanine dyes and their derivatives, possessing an alkyl substituents in the *meso* position of the polymethine chain (CH_3 , C_2H_5), studied by absorption and fluorescence spectroscopy are described in this paper.

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1. Introduction

Cyanines are the class of organic dyes discovered in 1856 by Williams. They are commonly used in numerous applications over wide areas of chemistry and technology [1]. One of the earliest and the most important adaptation of cyanine dyes (Cy) was their application in spectral sensitization and color photography [2,3]. Cy are also used in biomedicine [4] and laser technology [5]. Paired with borates, the effective electron donors, cyanines are used for photoinitiation of acrylate polymerization [6,7,8,9,10].

Symmetrical cyanines are the cationic dyes typically consisting of two hydrocyclic rings connected by an odd number of methine carbons. In most cases, the dyes adopt the “all-*trans*” geometry that

minimizes the steric interactions. The solid-state structures [11] and solution absorption measurements [12] of cyanine indicate that the steric interactions lead to a twisting of the methine group. Similarly, the crystal structures of *meso*-substituted (at the central atom of the methine chain) carbo-cyanines dyes [13] show that the steric crowding leads to the twisting of the methine chain. The examination of variable temperature ^1H NMR [14] and the electronic absorption spectra [15] indicate that these cyanine dyes are also twisted in the solution [1]. The electronic excitation with the visible light of an unaggregated cyanine dye leads to the formation of its excited singlet state $[\text{Cy}^+(\text{S}_1)]^*$. The lifetime and properties of $[\text{Cy}^+(\text{S}_1)]^*$ depend on the structure of the dye and on the medium in which the dye is dissolved. Typically, in nonviscous solvents, they exhibit the excited-state lifetime shorter than one nanosecond. Under these conditions the most important pathway for $[\text{Cy}^+(\text{S}_1)]^*$ deactivation is

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the rotation about a formal carbon–carbon double bond leading to the formation of a ground-state isomer [7]. West and Geddes reported that, at low temperatures in alcohols, the *meso*-substituted thiacyanines exhibit two absorption maxima, which are attributed to the all-*trans* and mono-*cis* isomers [15,16]. Similarly, Noukakis and co-workers conclude that unsubstituted thiacyanines, in general, present all-*trans* conformation. Bulky substituents at 9-position force the dyes to adopt the less sterically hindered mono-*cis* conformation. The ground state equilibrium between the all-*trans* and the mono-*cis* isomers was found to be dependent on the polarity of the solvent. It is shown that the mono-*cis* isomers are better stabilized in the polar solvents in contrast to the all-*trans* that are more stable in the low-polarity/highly polarizable solvents. The isomers absorb and emit at different wavelengths (the all-*trans* absorb and emit at longer wavelengths). The fluorescence of the mono-*cis* isomers is believed to be very shortlived, as the time-resolved fluorescence spectroscopy suggests [16]. For the *meso*-substituted dyes in solvents of low polarity the mechanism of the deactivation of the excited all-*trans* form involves a mono-*cis* isomer as an observable intermediate in the microsecond to millisecond time scale, whereas the deactivation of the excited mono-*cis* isomer is radiationless, avoiding essentially *cis*→*trans* photoisomerization [17]. Advances in the excited state lifetime measurements techniques allowed the more precise determination of the fluorescence decay of some cyanine dyes [18]. For trimethine indolocarbyanines, deviations from monoexponential decay kinetics have been observed and attributed to the presence of mono-*cis* and all-*trans* isomers [16]. It is generally accepted that the radiationless relaxation of the excited state of cyanine dyes is coupled with a torsional motion around the polymethine chain [16,19].

Cyanine dyes are the most commonly prepared as their halide or perchlorate salts [7]. It is well-known that they also form salts with various organoborate anions [7,20,21].

Borates are tetravalent, tetra-coordinate anionic boron-containing species. Torsell verified the tetrahedral structure of borates by synthesizing a chiral

example and recording its optical activity [1,22]. A more recent work has shown that tetraarylborates have significant voids or “crevices” between their substituents which permit occupation by suitably small cations such as planar cyanine dyes [1,20,21]. The occupation of the crevice by the cyanine dye gives a structure whose radius is less than the sum of the radii of individual ions. The intimate ion pairs of this nature are identified as penetrated ion pairs. The photophysical properties of cyanine borate penetrated ion pairs are dependent on the nature and structure of their anionic and cationic components [1]. The irradiation of the cyanine-borate ion pair with visible light generates the excited singlet state of the cyanine which can undergo three possible reactions, namely: *fluorescence, rotation to the photoisomer or the electron transfer to form the cyanine and boranyl radicals*.

In this paper, we describe the results of the investigation of the photophysical and photochemical properties of the selected cyanines, which are characterized by different chemical structures of the two heterocyclic moieties and a different structure of the polymethine bridge connecting the heterocycles (*meso*-substituted derivatives). The effect of a coupled counteranion structure on the properties of these dyes is described as well.

2. Experimental

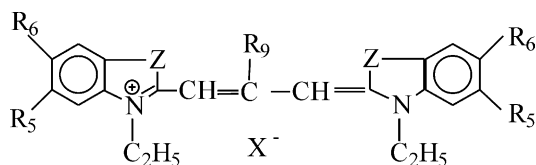
The chemical structure of the studied different cyanine dyes is given in Chart 1.

The substrates used for the preparation of the dyes and solvents were purchased from Fluka, Merck and Aldrich. The cyanine dyes and cyanine borates were prepared in our laboratory. The purity of the synthesized dyes was controlled by thin layer chromatography and their identity was checked by ¹H NMR, UV–vis and IR spectroscopy.

Electronic absorption spectra were recorded with a Varian Cary 3E Spectrophotometer and the fluorescence spectra were obtained using a Hitachi F-4500 Spectrofluorimeter. The absorption and emission spectra were recorded using the spectroscopic quality ethyl acetate and tetrahydrofuran, respectively, as the solvents. The measurements

were performed at ambient temperature. The fluorescence quantum yield ϕ_f of thiacyanobocyanine dyes in THF solution was determined using optically matched samples of Rhodamine B ($\phi_f = 0.5$) in ethanol with absorbances of 0.1 at $\lambda_{\text{EXC}} = 530$ nm (1 cm path length) as a reference. The fluorescence quantum yield of oxacyanobocyanine dyes in THF solution was determined using Fluoresceine in ethanol as a reference with ($\phi_f = 0.93$, $\lambda_{\text{EXC}} = 488$ nm) and optically matched samples having absorbances of 0.1 at λ_{EXC} (path length of 1 cm).

Fluorescence lifetime measurements were performed using pico/femtosecond spectrometer constructed at Adam Mickiewicz University, Poznań (Poland). The design and construction of a spectrometer for picosecond fluorescence decay measurements are described elsewhere [23,24]. The apparatus utilizes for the excitation a pico/femtosecond tunable Ti:Sapphire laser generating pulses of about 1 ps. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals in the range of single picoseconds possible. The dyes were studied at concentration able to provide equivalent absorbancies at 460 or 480 nm (0.2–0.4 in the 10 mm cell) to be obtained. ^1H NMR spectra were obtained with a 200 MHz NMR Spectrometer Gemini 2000.



$Z = \text{S}, \text{O}$

$R_5 = \text{H}, \text{Cl}, \text{F}, \text{CH}_3, \text{CH}_3\text{O}, \text{C}_6\text{H}_5, \text{NO}_2, \text{NH}_2, \text{OH}$

$R_6 = \text{H}, \text{CH}_3\text{O}, \text{C}_2\text{H}_5\text{O}, \text{Cl}, \text{Br}$

$R_9 = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$

Chart 1. General chemical formula of thia- and oxacyanobocyanine dyes tested.

3. Results and discussion

3.1. Synthesis

3.1.1. Cyanine dyes

For the study 32 various symmetrical cyanine dyes were obtained by the condensation of cycloammonium salts with corresponding *ortho*-ester. The general scheme of the synthesis of the studied oxacyanobocyanine and thiacyanobocyanine dyes was reported previously [25]. The dyes were prepared according to the procedure given by Hamer [26]. Eight of the synthesized dyes are not described in the literature, yet.

3.1.1.1. 5,5'-Dichloro-3,3',9-triethylcarbocyanine iodide. A solution of 1 mmol of 5-chloro-3-ethyl-2-methylbezoxazole iodide and 2 mmol of triethyl orthopropionate in 10 ml pyridine was refluxed for 2 h. The solvent was removed in a vacuum, and the dark solid residue was recrystallized from ethanol to yield 34% of the dye as purple needles, mp 174 °C, ^1H NMR (200 MHz, DMSO) δ ppm: 0.884–0.912 (3H); 1.068–1.104 (6H); 4.268–4.300 (2H); 4.268–4.688 (4H, N-CH₂-); 6.944–6.988 (d, 2H, -CH=); 7.921 (2H); 7.409–7.451 (2H); 7.778–7.821 (2H).

3.1.1.2. 3,3'-Diethyl-5,5'-dimethylcarbocyanine iodide. A solution of 0.02 mol of 3-ethyl-2,5-dimethylbezoxazole ethylsulfate and 0.04 mol of triethyl orthoformate in 5 ml pyridine with five drops of acetic anhydride was refluxed for 2.5 h. The solvent was removed in a vacuum and the dark solid residue was dissolved in methanol and the dye was precipitated by 30 ml of 5% KI in methanol. The crystals were collected by the vacuum filtration. The product was recrystallized from ethanol giving 1.35 g (13.5%) of the dye as gold-red needles, mp 278–280 °C, ^1H NMR (200 MHz, DMSO) δ ppm: 1.315–1.385 (6H); 1.013–1.083 (6H); 4.160–4.230 (d, 4H, N-CH₂-); 6.016–6.084 (d, 2H, -CH=); 7.184–7.225 (d, 2H); 7.529 (2H); 7.605–7.646 (d, 2H); 8.262 (1H).

3.1.1.3. 3,3'-Diethyl-5,5',9-trimethylcarbocyanine ethylsulfate. A solution of 0.007 mol of 3-ethyl-2,5-dimethylbezoxazole ethylsulfate and 0.014 mol

of triethyl ortoacetate in 0.02 mol of pyridine and 0.014 mol of glacial acetic acid was refluxed for 3 h. The solvent was evaporated in a vacuum and the remaining dark solid was recrystallized from ethanol. The crystals were filtered to yield 0.35 g (18.9%) of the dye as purple needles, mp 242 °C, ^1H NMR (200 MHz, DMSO) δ ppm: 1.062–1.098 (3H); 2.480–2.498 (6H); 2.625 (3H); 3.215–3.250 (6H); 3.718–3.753 (2H); 4.221–4.254 (d, 4H, N-CH₂-); 7.155–7.519 (d, 2H, -CH=); 7.519–7.633 (4H); 8.161 (2H).

3.1.1.4. 3,3',9-Triethyl-5,5'-dimethylcarbocyanine iodide. A solution of 0.007 mol of 3-ethyl-2,5-dimethylbezoxazole ethylsulfate and 0.014 mol of triethyl ortopropionate in 0.02 mol of pyridine and 0.014 mol of glacial acetic acid was refluxed for 3 h. The solvent was removed in a vacuum and to the residue a solution of 5% KI in methanol (30 ml) was added causing a precipitation of the dark crystals, which were recrystallized from ethanol and filtered yielding 0.33 g (17.2%) of the dye as red needles, mp 261–262 °C, ^1H NMR (200 MHz, DMSO) δ ppm: 1.042–1.124 (3H); 1.267–1.381 (12H); 3.667–3.774 (2H, CH₂-CH₃); 4.239–4.273 (d, 4H, N-CH₂-); 7.174–7.215 (2H, -CH=); 7.538 (2H); 7.615–7.655 (4H).

3.1.1.5. 3,3'-Diethyl-5,5'-dimethoxycarbocyanine iodide. A solution of 0.0036 mol of 3-ethyl-5-methoxy-2-methylbezoxazole ethylsulfate and 0.0072 mol of triethyl ortoformate in 1 ml pyridine and 0.5 ml of acetic acid was refluxed for 3 h. The solvent was evaporated in a vacuum and the dark solid was precipitated from methanol by addition of 30 ml of 5% KI in methanol. The crystals were collected by a vacuum filtration. The product was recrystallized from ethanol with the yield of reaction 42%. The dye was obtained as red-purple needles, mp 287–288 °C, ^1H NMR (200 MHz, DMSO) δ ppm: 1.310–1.382 (6H); 3.845 (6H, CH₃O); 4.211–4.248 (d, 4H, N-CH₂-); 6.006–6.073 (d, 2H, -CH=); 6.903–6.960 (2d, 2H); 7.337–7.349 (2d, 2H); 7.624–7.669 (2d, 2H); 8.235 (1H).

3.1.1.6. 3,3'-Diethyl-5,5'-dihydroxy-thiacarbocyanine ethylsulfate. A solution of 0.006 mol of 3-ethyl-5-hydroxy-2-methylbenzothiazole

ethylsulfate in 0.018 mol of pyridine was refluxed for 10 min. Then a mixture of 0.012 mol of triethyl ortoformate and 0.012 mol of glacial acetic acid was added to the reaction medium. The mixture was refluxed for 3 h. After cooling, the precipitated green plates crystals were collected by a vacuum filtration. The yield of reaction was 1.03 g (65%), mp 262–263 °C, ^1H NMR (200 MHz, DMSO) δ ppm: 1.064–1.136 (3H); 1.268–1.455 (6H); 4.250–4.283 (d, 4H, N-CH₂-); 4.580–4.688 (2H, CH₂-O); 6.493–6.556 (d, 2H, -CH=); 6.822–6.874 (2H); 7.053 (2H); 7.532–7.732 (2H); 8.161–8.206 (1H); 10.164 (2H).

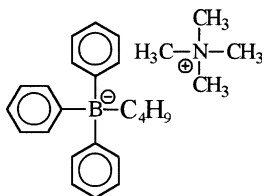
3.1.1.7. 3,3'-Diethyl-5,5'-dihydroxy-9-methylthiacarbocyanine ethylsulfate. A solution of 0.006 mol of 3-ethyl-5-hydroxy-2-methylbenzothiazole ethylsulfate in 0.018 mol of pyridine was refluxed for 10 min. Next to the obtained mixture 0.012 mol of triethyl ortoacetate and 0.012 mol of glacial acetic acid were added. The resulting mixture was refluxed for 3 h. After cooling, the crystals were collected by a vacuum filtration (yield 50%) giving the dye as black crystals, mp 241–242 °C, ^1H NMR (200 MHz, DMSO) δ ppm: 1.340–1.410 (9H); 1.491–1.561 (3H); 3.718–3.753 (2H); 4.499–4.654 (4H, N-CH₂-); 6.519 (2H, -CH=); 6.875–6.930 (2H); 7.096–7.151 (2H); 8.035–8.079 (2H); 10.218 (1H); 10.482 (1H).

3.1.1.8. 3,3',9-Triethyl-5,5'-dihydroxy-thiacarbocyanine ethylsulfate. A solution of 0.006 mol of 3-ethyl-5-hydroxy-2-methylbenzothiazole ethylsulfate in 0.018 mol of pyridine was refluxed for 10 min. After adding 0.012 mol of triethyl ortopropionate and 0.012 mol of glacial acetic acid to the resulting mixture the solution was refluxed for 3 h. After cooling, the crystals were filtered to give 0.5 g (30%) of the dye as dark green plates, mp 232–233 °C, ^1H NMR (200 MHz, DMSO) δ ppm: 1.063–1.135 (3H); 1.272–1.418 (9H); 2.885–2.923 (2H); 3.686–3.793 (2H); 4.396–4.430 (d, 4H, N-CH₂-); 6.411 (2H, -CH=); 6.878–6.931 (2H); 7.122–7.131 (2H); 7.798–7.842 (2H); 10.221 (2H).

3.1.2. Borates

The synthesis of tetramethylammonium *n*-, *sec*-, *tert*-butyltriphenylborate salts were carried out

following the guidelines given by R. Damico [27] (for example the structure of tetramethylammonium butyltriphenylborate).



Alkyltriphenylborates as their tetramethylammonium salts were prepared by the reaction of an alkylmetal (generally, lithium or magnesium) with triphenylboron. The exchange of the metal cation on tetramethylammonium bromide gives the ammonium salts of borates as stable, colorless solids [7,21].

3.1.2.1. Tetramethylammonium *n*-butyltriphenylborate (B2). Triphenylboron was sublimated at 140 °C to yield a white solid. 6.4 ml of 1.6 M *n*-butyllithium in 40 ml of hexane was added to 2.5 g (0.01 mol) of triphenylboron dissolved in 20 ml of benzene. A white solid formed was filtered, washed with two 50-ml portions of pentane and dried at 30 °C (0.1 mm) for 1 h. The product was dissolved in 50 ml of water and added to a saturated solution of tetramethylammonium bromide in water. A white precipitate was immediately visible. The mixture was stirred for 0.5 h, filtered and washed until the washing showed no trace of bromide ion. The resulting solid was dried to yield 82%, mp 251–253 °C (mp 325 °C for lithium salts [27]), ¹H NMR (DMSO) δ (ppm): 0.703–0.774 (3H), 1.125–1.193 (6H), 3.067 (12H), 6.686–6.756 (3H), 6.844–6.914 (6H), 7.166–7.201 (6H).

3.1.2.2. Tetramethylammonium *sec*-butyltriphenylborate (B3). The synthesis was carried out by the method described above. The 1.3 M solution of *sec*-butyllithium in hexane was used as a substrate. The yield of reaction was 81%, mp higher than 260 °C, ¹H NMR (DMSO) δ (ppm): 0.552–0.580 (2H); 0.792–0.865 (6H); 1.100–1.200 (1H); 3.069 (s, 12H, N(CH₃)₄); 6.715–6.751 (3H); 6.852–6.924 (6H); 7.243–7.279 (6H). This compound was not described earlier.

3.1.2.3. Tetramethylammonium *tert*-butyltriphenylborate (B4). The synthesis was also carried out by the method described above. The 1.7 M solution of *tert*-butyllithium in hexane was used for the synthesis. The yield of reaction was 93%, mp 134–138 °C, ¹H NMR (DMSO) δ (ppm): 0.824–0.837 (9H); 3.057 (s, 12H, N(CH₃)₄); 6.771–6.993 (9H); 7.216–7.337 (6H).

The last compound (B4) is not described earlier.

3.1.2.4. Tetramethylammonium tetra-*n*-butylborate (B5). The compound was prepared by the method given by Murphy [21]. The 30 ml of 2.5 M *n*-butyllithium solution in hexane was dissolved in 30 ml of ether at 0 °C. To this solution 2 ml of freshly distilled boron trifluoride etherate was added and the resulting solution was stirred for 3 h at 0 °C. The mixture was allowed to warm slowly to the room temperature and then stirred overnight. After evaporation of the solvent, the saturated solution of tetramethylammonium bromide in water was added to the residue. The white solid was collected by a vacuum filtration and dried. The yield of reaction was 55% (78% [21]), mp 115–117 °C (106–112 °C [21]), ¹H NMR (DMSO) δ (ppm): 0.776–0.921 (12H); 1.144–1.435 (24H); 3.446 (12H, N(CH₃)₄). This compound is not described earlier, either.

3.1.3. Cyanine borates

General method: The equimolar amounts of tetramethylammonium alkyltriphenylborate and the cyanine dye as iodide or ethylsulfate salt were dissolved in warm acetonitrile. Water was slowly added to the warm solution until the small amount of a precipitate was formed then a small amount of acetonitrile was added to clarify. Next the mixture was allowed to cool in the dark. The precipitated cyanine borate was filtered out [1].

3.2. Spectroscopic and physical properties of cyanine dyes

Generally, cyanine dyes are present in solution at room temperature as the ground state all-*trans* isomers. These compounds are characterized by a truly complex pattern of photophysical properties. Their decay from the initially reached first excited

Table 1

The structures and spectroscopic properties of thia- and oxacarbo-cyanine dyes tested

Dye	Substitution			λ_{AB}	λ_{EM}	τ_s	τ_s	τ_s	τ_s	τ_s
	C5	C6	C9	[nm] EtAc	[nm] THF	[ps] CyX	[ps] CyB2	[ps] CyB3	[ps] CyB4	[ps] CyB5
Cy3	H	H	H	556 ^a	582	139.09 391.93	122.34 248.16	129.59 275.8	134.9 281.79	
Cy4	H	H	CH ₃	542 ^a	579.4	22.21	16.53		17.12	
Cy50	H	H	C ₂ H ₅	562	575.6 ^b	51.42		16.95	32.82	
Cy8	F	H	H	562 ^a	592.8	166.91 420.6	155.94 355.06		163.08 368.95	161.51 427.1
Cy56	F	H	CH ₃	561	585 ^c	34.19	20.44		22.11	22.14
Cy57	F	H	C ₂ H ₅	567	583.8 ^c	77.29				
Cy9	CH ₃	H	H	564 ^a	593.6	187.84 560.14	173.92 354.9			
Cy46	CH ₃	H	CH ₃	561	582.6 ^c	—	15.31			
Cy47	CH ₃	H	C ₂ H ₅	567	584 ^c	77.78	51.66	74.13	52.78	
Cy10	H	CH ₃ O	H	572 ^a	597.2	215.68 33.31	189.86 380.93			160.62 504.75
Cy61	CH ₃ O	H	H	584	602.8 ^c	109.15 531.84	185.14			
Cy11	CH ₃ O	H	C ₂ H ₅	564 ^a	600	114.27 367.87	34.08 156.48		8.76 134.72	
Cy33	H	C ₂ H ₅ O	H	580 ^a	599.8	46.41 367.34	158.78 347.57			181.84 398.02
Cy36	NO ₂	H	H	556 ^a	584.6	41.21 187.92	26.11 121.22		38.9 122.52	
Cy58	OH	H	H	580	605.8 ^c	45.4 191.06	44.61 363.03		34.63 230.93	
Cy59	OH	H	CH ₃	567	602.2 ^c	105.04	13.3			80.98
Cy60	OH	H	C ₂ H ₅	564	600.8 ^c	133.81 595.6	18.11			
Cy63	H	Cl	H	574	591.4	127.6 400.97			188.71 376.84	
Cy65	H	Cl	CH ₃	564	579.8 ^c	38.82				28.78
Cy66	H	Cl	C ₂ H ₅	569	581.6 ^c	88.31		60.12		
Cy64	H	Br	H	574	585.8 ^c	117.73 422.55				
Cy19	H	H	H	482 ^a	507.2	94.95 233.55	62.57 175.7		67.23 174.59	
Cy41	H	H	CH ₃	494	512.6	32.16	25.85			
Cy45	H	H	C ₂ H ₅	496	514.2 ^a	48.84 48.85	30.15	33.5		39.85 7.31
Cy22	Cl	H	H	488 ^a	509	68.14 255.61	72.26 244.02	50.37 351.11		109.92 328.74
Cy48	Cl	H	CH ₃	500	515 ^c	83.45 688.89	47.163 166.4			
Cy49	Cl	H	C ₂ H ₅	501	518.4 ^c		36.52	14.85 50.48		
Cy23	CH ₃	H	H	488 ^a	511	89.13 229.62	80 220.2	81.24 227.65		74.99 238.25
Cy51	CH ₃	H	CH ₃	500	518.6 ^c	71.42 29.35				
Cy53	CH ₃	H	C ₂ H ₅	501	519.4 ^c		31.05			

Table 1 (continued)

Dye	Substitution			λ_{AB}	λ_{EM}	τ_s	τ_s	τ_s	τ_s	τ_s
	C5	C6	C9	[nm] EtAc	[nm] THF	[ps] CyX	[ps] CyB2	[ps] CyB3	[ps] CyB4	[ps] CyB5
Cy24	CH ₃ O	H	H	498 ^a	520.2	129.46 342.13	119.59 318.04	113.96 301.46		
Cy27	CH ₃ O	H	C ₂ H ₅	504 ^a	528.2	16.8 45.56	15.19 51.76	19.05 54.38		22.39 69.53
Cy25	C ₆ H ₅	H	H	494 ^a	529.4	140.03 399.17	86.07 362.32	109.21 358.61	92.23 370.91	
Cy52	C ₆ H ₅	H	CH ₃	506	522.8 ^b	29.27 86.25	58.53	57.03		31.45 80.07
Cy28	C ₆ H ₅	H	C ₂ H ₅	502 ^a	526.6	23.64 110.34	37.11 97.25		31.32 94.3	31.21 116.0

The compounds numbered from **Cy3** to **Cy64** represent the thiocarbocyanine dyes and from **Cy19** to **Cy28** oxacarbocyanine dyes, respectively. The symbols X, B2, B3, B4 mean: iodide or ethyl sulfate anion, *n*-butyltriphenylborate or *sec*-butyltriphenylborate or *tert*-butyltriphenylborate anions, respectively.

^a Recorded in methanol.

^b Recorded in ethyl acetate.

^c Recorded in DMF.

state is the result of several competing processes: non-radiative (intersystem crossing to the triplet state, photoisomerization around the double bonds of the flexible polymethine chain and the thermal back isomerization) or radiative (fluorescence) return to the ground state. It is well known that thiocarbocyanine monomers without *meso*-substituent at the polymethine chain exhibit a moderate fluorescence quantum yield (ϕ_f), a low quantum yield of intersystem crossing (ϕ_{ISC}), (for example ϕ_{ISC} has been reported to be $<10^{-3}$ for **Cy3** [28]) and a rather high yield of *trans*→*cis* photoisomerization ($\phi_{t\rightarrow c}$). However, virtually no photoisomerization takes place for thiocarbocyanines with a *meso* alkyl substituent in polar solvents since they exhibit a shift from the *trans* to a *cis* form in the ground state on increasing the solvent polarity [29].

As the relative mass of the individual photo-processes is dependent on the chemical structure of the cyanine dyes [30], therefore we selected some representatives of the two classes of cyanines, (e.g. thiocarbo and oxacarbo derivatives and their *meso*-substituted analogues see Table 1) for the characterization of their photophysical and photochemical properties.

It is accepted that for thiocarbocyanine dyes the singlet state mechanism of *trans*→*cis* photoisomerization is operating [17] except of Serpone

and Sahyom [31] who argued in favor a triplet mechanism on the basis of ϕ_{ISC} value of 0.55 in dichloromethane.

According to the Chibisov's studies it is known that the *trans*→*cis* photoisomerization is absent for alkyl substituted in the *meso*-position thiocarbocyanine dyes and that the intersystem crossing to the triplet state does not play a significant role in the deactivation of the excited singlet state [28].

This feature can be illustrated by the laser flash photolysis of *N,N*→-dimethyldimethylindocarbocyanine hexafluorophosphate [**Cy**⁺**PF**₆[−]] that reveals the formation of several transient intermediates, especially an intermediate characterized by the absorption band with apparent maxima at 580 nm which is assigned to the photoisomer formed by the rotation about one of the central bonds of **Cy**⁺. A similar photoisomerization has been observed for a wide range of cyanine dyes. The mono-*cis* photoisomer regenerates *trans* [**Cy**⁺] by a thermal process over a period of several microseconds. As it was previously noted, for the related cyanine dyes, there is no evidence for the formation of the triplet state of cyanine [**Cy**⁺(T)] *via* ISC process in the direct irradiation of **Cy**⁺**PF**₆[−] [7,17].

The structure and spectroscopic properties of thia- and oxacarbocyanine dyes tested in this work

are summarized in Table 1. The investigated dyes have an intensive absorption band located in the range of 550–600 nm for the thiocarbocyanine dyes and 450–500 nm for oxacarbocyanines. The second band is less intensive and shifted to the blue region of spectrum of about 60–70 nm (Table 1). The position of absorption maximum does not depend on the type of a borate anion used as counterion.

The series of the tested dyes contain several so called *meso* substituted analogous. The substantial difference observed between cyanine and its *meso* analogue is visible in a value of the molar absorption coefficient. For alkyl substituted *meso* dyes the value of the molar absorption coefficient is about one order of magnitude lower than for the non-substituted derivatives. From literature it is known that the introduction of an alkyl substituent into the *meso* position causes a destabilization of the dye all-*trans* isomer in solution and this in turn leads to a decrease of the electronic absorption intensity [18,19].

The fluorescence spectra of the tested cyanines are roughly a mirror image of the absorption spectra. The typical absorption and emission spectra of the investigated dyes are shown in Fig. 1.

During the fluorescence measurements it was found that the fluorescence maximum does not depend on the fluorescence excitation wavelength. The fluorescence emission in THF exhibits a max-

imum red-shifted in comparison to the absorption maximum by less than 1000 cm^{-1} (Table 1). The value of Stokes shift only slightly depends on the type of the borate ion and it is the highest for *n*-butyltriphenylborate anion. Since the Stokes shift is no large and the half width of the absorption and emission bands are almost the same, therefore, one can conclude that the geometry of the dye molecule and the charge distribution is in its both ground and emitting excited states almost the same.

Most cyanines listed in Table 1 show a fluorescence quantum yield lower than 0.1 for thiocarbocyanines and lower than 0.5 for oxacarbocyanines, indicating a predominantly non-radiative decay from the lowest excited singlet state (Table 2). The fluorescence lifetimes of the simplest thiocarbocyanine dye (Cy3) in a mixture of ethyl acetate:1-methyl-2-pyrrolidyn-2-one (9:1) are equal: $\tau_f=0.3$ ns and 0.14 ns with quantum yield $\phi_f=0.046$ in THF. The simplest oxacarbocyanine dye (Cy19) singlet state lifetime is about 0.1 ns and $\phi_f=0.12$.

In general, the fluorescence quantum yields of thiocarbocyanine dyes are smaller than for the corresponding oxacarbocyanines. It is noteworthy that the ϕ_f value of Cy3 measured in our laboratory is in a good agreement with this given in the literature [17].

As it was mentioned in the introduction, the irradiation of the cyanine borates with visible light generates the excited singlet state of cyanine which can undergo three possible reactions: fluorescence, rotation to a photoisomer or the electron transfer. There is not observed a distinct influence of the borate anion type on the quantum yield of fluorescence. However, it should be noted that the fluorescence quantum yield of *meso*-substituted cyanine dyes is about one order of magnitude lower than for non-substituted analogues (see Table 2). On the basis of the above observation one can conclude that a non-radiative deactivation processes play a dominant role in the deactivation of the excited singlet state of *meso*-substituted cyanine dyes.

The fluorescence lifetime and the quantum yield are related to the radiative (k_r) and non-radiative (k_{nr}) rate constants by the photophysical Eqs. (1) and (2) [32]:

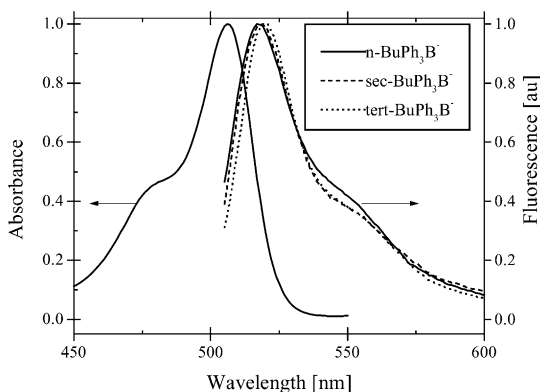


Fig. 1. Absorption and emission spectra of Cy52 (3,3'-diethyl-5,5'-diphenyl-9-methylthiocarbocyanine salts) in ethyl acetate.

Table 2
The fluorescence quantum yield of thia and oxacarbocyanine dyes in THF

	Anion					
	I	C ₂ H ₅ SO ₄	B2	B3	B4	B5
<i>Thiacarbocyanine dye</i>						
Cy3	0.046		–	0.072	0.056	0.080
Cy4	0.003		0.003	0.003	0.006	0.006
Cy8	0.016	0.087	0.068	0.065	0.060	0.090
Cy9		0.056	0.058	0.067	0.071	0.100
Cy10	0.021	0.068	0.048	0.054	0.047	0.070
Cy11	0.048		0.017	0.019	0.019	0.032
Cy33	0.048		–	–	0.021	0.046
Cy36		0.032	–	0.041	–	–
Cy46		0.0055		–	0.0035	0.0051
Cy47		0.0084		0.0071	0.010	0.011
Cy50	0.0035			0.037		
Cy56	0.0029	0.0081		0.041	0.0061	0.0092
Cy57		0.016				0.012
Cy58	0.007	0.040	0.022		0.0016	0.010
Cy59	0.0054	0.0051				
Cy60		0.0048				0.0042
Cy61		0.046	0.069	0.072	0.096	0.087
Cy63	0.016	0.089			0.051	0.082
Cy64	0.064				0.056	
Cy65		0.015				0.010
Cy66		0.037		0.019		0.013
<i>Oxacarbocyanine dye</i>						
Cy19	0.121		0.227	0.231	0.235	0.217
Cy22	0.180		0.307	0.329	0.311	0.333
Cy23	0.139		0.250	0.249	0.252	0.247
Cy24			0.271	0.280	0.280	
Cy25	0.271		0.441	0.429	0.444	0.429
Cy27	0.060		0.074	0.051	0.060	0.071
Cy28	0.089		0.051	0.056	0.052	
Cy41	0.024		0.027	0.027	0.029	0.030
Cy45	0.035		0.029	0.030	0.032	0.037
Cy48	0.021		0.031			
Cy49	0.029		0.039	0.039		
Cy51	0.058	0.087	0.030	0.030	0.035	0.059
Cy52	0.15	0.16	0.053	0.057		0.082
Cy53	0.039		0.033	0.042	0.044	0.037

$$k_r = \frac{\phi_f}{\tau_f} \quad (1)$$

$$k_{nr} = \frac{1 - \phi_f}{\tau_f} \quad (2)$$

Upon substituting the measured fluorescence lifetimes and fluorescence quantum yields, it is calculated that, for thiacarbocyanines $k_r = (0.07–$

$2.18) \times 10^9 \text{ s}^{-1}$ and $k_{nr} = (5.01–112) \times 10^9 \text{ s}^{-1}$ and $k_r = (0.25–6.53) \times 10^9 \text{ s}^{-1}$ and $k_{nr} = (5.21–132) \times 10^9 \text{ s}^{-1}$ for oxacarbocyanines, respectively (Table 3).

This estimation indicates that for thiacarbocyanine dyes the non-radiative transition rate is about two orders of magnitude faster than the radiative rate but only three times faster for oxacarbocyanines. From the inspection of the data presented in Table 3, one can conclude that for *meso*-sub-

Table 3

The radiative (k_r) and non-radiative (k_{nr}) rate constants measured for tested cyanine dyes

Dye	X			B2			B3			B4			B5		
	$k_r/10^9$ [s ⁻¹]	$k_{nr}/10^9$ [s ⁻¹]	k_r/k_{nr}	$k_r/10^9$ [s ⁻¹]	$k_{nr}/10^9$ [s ⁻¹]	k_r/k_{nr}	$k_r/10^9$ [s ⁻¹]	$k_{nr}/10^9$ [s ⁻¹]	k_r/k_{nr}	$k_r/10^9$ [s ⁻¹]	$k_{nr}/10^9$ [s ⁻¹]	k_r/k_{nr}	$k_r/10^9$ [s ⁻¹]	$k_{nr}/10^9$ [s ⁻¹]	k_r/k_{nr}
Cy3	0.33	6.86	20.7				0.56	7.16	12.9	0.41	7.0	16.8			
Cy8	0.09	5.9	61.5	0.04	5.98	13.7				0.37	5.76	15.7	0.56	5.63	10.1
Cy9	0.1	5.03	50.2	0.33	5.42	16.2									
Cy10	0.63	29.4	46.6	0.25	5.01	19.8							0.44	5.79	13.3
Cy11	0.42	8.33	19.8	0.5	28.8	57.8				2.17	112	51.6			
Cy33	1.03	20.5	19.8										0.25	5.25	20.7
Cy50	0.07	19.4	285				2.18	56.8	26.0						
Cy56	0.08	29.2	344							0.28	45	163	0.42	44.8	107.7
Cy63	0.12	7.71	61.5							0.27	5.03	18.6			
Cy19	1.27	9.26	7.26	3.63	12.4	3.4				3.5	11.4	3.25			
Cy22	2.64	12	4.55	4.25	9.59	2.26	6.53	13.3	2.04				3.03	6.07	2.0
Cy23	1.56	9.66	6.19	3.13	9.83	3	3.06	9.24	3.01				3.29	10	3.05
Cy24				2.27	6.1	2.69	2.46	6.32	2.57						
Cy25	1.94	5.21	2.69	5.12	6.49	1.27	3.93	5.23	1.33	4.81	6.03	1.25			
Cy28	3.76	38.5	10.2	0.52	9.76	18.6				1.66	30.3	18.2			
Cy41	0.75	30.3	40.7	0.11	4.0	36									
Cy45	0.72	19.8	27.6	0.96	32.2	33.5	0.9	29	32.3				5.06	132	26.03
Cy48	0.25	11.7	46.6	0.66	20.5	31.2									
Cy49				1.07	26.3	24.6	2.63	64.7	24.6						
Cy51	0.81	13.2	16.2												
Cy52	5.12	29	5.67	0.90	16.2	17.9	0.99	16.5	16.5				1.02	11.5	11.19

The symbols X, B2, B3, B4 mean: iodide or ethyl sulfate anion, *n*-butyltriphenylborate or *sec*-butyltriphenylborate or *tert*-butyltriphenylborate anions, respectively.

stituted cyanine dyes the non-radiative processes are much more effective than the radiative ones.

The discussion about the electron transfer process occurring between cyanine cation and borate anion requires the knowledge of several data described by Rehm–Weller equation. These are: the reduction potential (E_{red}) of dye, the oxidation potential of borate anion (E_{ox}), the fluorescence lifetime (τ_s) and the energy of excited state singlet (E_{00}). The part of these data was presented in our earlier papers [8,25,33].

The kinetics of the quenching of the excited singlet state was studied by the measurements of the fluorescence lifetime for the selected group of the cyanine dyes. These measurements were carried out in the mixture composed of ethyl acetate and 1-methylpyrrolidyl-2-one (9:1). The examples of the fluorescence decay curves are shown in Fig. 2.

The analysis of the experimental data shows that there is a significant difference between the lifetime of cyanine dye with and without an alkyl group in *meso* position of the polymethine chain. The effect of ethylene sulfate ion exchange on borate ion is illustrated in Fig. 3.

The lifetime of the excited singlet state of cyanine dyes strongly depends on the structure of the dye and the type of a borate ion (see Table 1). The experimental results showed that the lifetimes of the excited singlet state of thiacyanoborane dyes

tested oscillate in the range from 3 to 593 ps. The lifetimes of the excited singlet state of the oxacyanoborane dyes are shorter.

The hindered rotation about of each bond of the polymethine chain, caused by introducing the methyl group in *meso* position, dramatically decreases the fluorescence lifetime. It is attributed to a faster relaxation to the ground state of the excited dye. The measured values of the excited singlet state lifetime for the studied cyanine salts are also collected in Table 1.

For the majority of the dyes the lifetime measurements show two-exponential fits with the experimental residual very close to the theoretical one. There are also, mostly for *meso*-cyanines, evidences of mono-exponential decay previously reported for thiacyanoborane [17,31].

It was also our intention to extend the knowledge about the specific photophysical properties of the excited singlet state of cyanine dyes. The quantum chemical calculations indicate that the dye ground states are exceptionally symmetrical. This specific behavior is illustrated by the data summarized for the simplest oxacyanoborane dye in Table 4.

The results obtained by the AM 1 calculations show that for the all-*trans* conformers the bonds formed between the C_8 or $C_{8'}$ and C_9 are non-differentiated. Similar properties indicate bonds C_2 – C_8 and C_2 – $C_{8'}$. This finding allows to conclude that

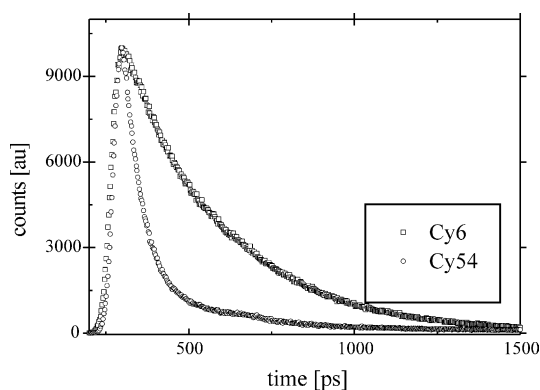


Fig. 2. The influence of the substitution in *meso* position on the fluorescence lifetime of cyanine borates tested. Fluorescence measurements performed for the dyes in MP–EtAc solution (1:9). The structures of presented dyes are shown in our previous paper [33].

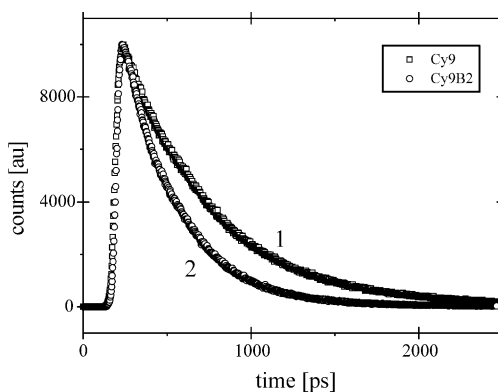
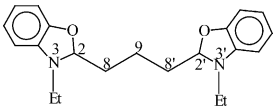
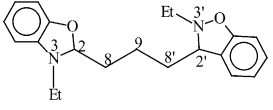
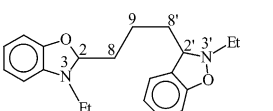
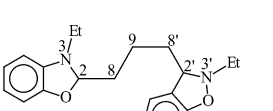
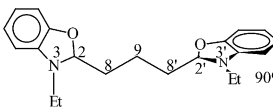


Fig. 3. Influence of the borate ion (*n*-butyltriarylborate) on the fluorescence intensity decay recorded for Cy9. Fluorescence measurements performed for the dyes in MP–EtAc solution (1:9).

Table 4

The enthalpy of molecule formation and electron density calculated for geometric and conformational isomers of the simplest oxacarbocyanine dye

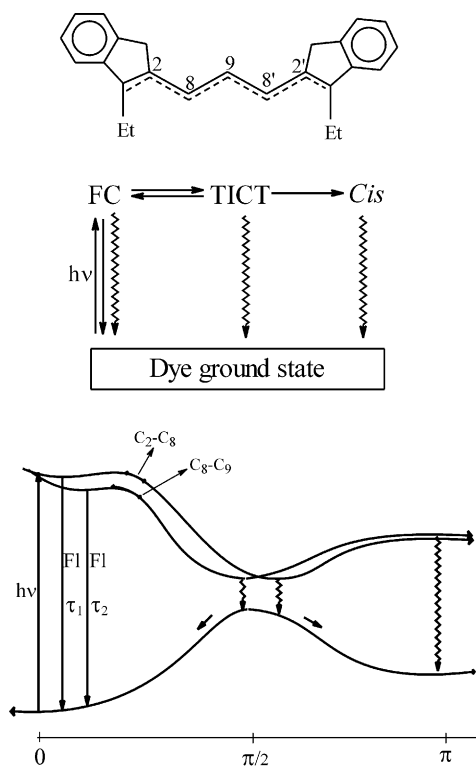
Dye structure	$\Delta_f H$ kJ/mol ⁻¹	Electron density						
		2	2'	3	3'	8	8'	9
	869.0	0.287	0.285	-0.173	-0.181	-0.330	-0.335	0.112
	860.6	0.283	0.285	-0.173	-0.181	-0.337	-0.334	0.130
	911.3	0.306	0.249	-0.131	-0.195	-0.309	-0.356	0.105
	895.0	0.289	0.288	-0.177	-0.179	-0.337	-0.335	0.138
	921.03	0.283	0.350	-0.196	-0.123	-0.377	-0.414	0.107

the mono-*cis* form of the dye can be formed either by the twisting of the C₈–C₉ or C_{8'}–C₉ bonds. The twisting around C₂–C₈ and C_{2'}–C_{8'} bonds, according to Görner et al. [17] give also *cis*-isomer, however, energetically these conformers differ from that obtained by the rotation of C₈–C₉ or C_{8'}–C₉ bonds. The results obtained by the AM 1 calculations gave a rough guideline regarding the energies of possible ground state conformers (see Table 4). Very recently Robb and Olivucci described CASSCF quantum chemical calculations for the lowest singlet excited state of cyanine dye models of different chain lengths [34,35]. On the basis of these calculations they concluded that pentamethine cyanine dye may undergo *trans*–*cis* photoisomerization about C₂–C₈ (C_{2'}–C_{8'}) and C₈–C₉ (C_{8'}–C_{9'}) bonds. Based on Robb and Olivucci's calculations as well as on ours, for the

explanation of the fluorescence biexponential decay of the tested dyes, we propose the following kinetic model (Scheme 1).

After excitation, the relaxed Franck–Condon state FC is reached. This state can emit or form a twisted structure (TICT) with a different twisted angle (about 100°) for the rotation about C₂–C₈ (C_{2'}–C_{8'}) and C₈–C₉ (C_{8'}–C_{9'}) bonds. This configuration corresponds with the minimum on the potential surface of the lowest excited singlet state. The excited state potential energy minimum is reflected in the ground state potential surface, which leads to the occurrence of conical intersections of potential energy surfaces. Such an intersection provides a universal decay route for the excited conjugated, polyatomic molecules. Since the activation energy for the twist about C₂–C₈ (C_{2'}–C_{8'}) bond and C₈–C₉ (C_{8'}–C_{9'}) bond differs,

therefore one can expect that the time needed for the formation of the TICT state is different for molecules with a rotation about C_2-C_8 ($C_2-C_{8'}$) bond in comparison to the time related with the rotation about C_8-C_9 ($C_{8'}-C_{9'}$) bond. A subsequent twist leads to the formation of non-emitting *cis* form of the dye. The twisting about C–C bond results in the formation of two decoupled π fragments with an odd and even number of carbon atoms, respectively. At a conical intersection the positive charge is completely localized on the fragment with an odd number of carbon atoms and a negative charge is located on the fragment with an even number of carbon atoms. This leads to the formation of a polar molecule. Any emission from this type of excited molecule should exhibit large Stokes shift. It has been mentioned earlier that the fluorescence spectra of the tested cyanine show a classical image of the absorption spectra with Stokes shift ranging from 350 to 650 cm^{-1} . This observation permits to conclude that the TICT state is the non-emitting state.



Scheme 1. Dye ground state.

The spectroscopic properties of the *cis* form of cyanine dyes should also be clarified here. In literature, there is a controversy related to the interpretation of the transient absorption spectra of cyanine dyes. Indocarbocyanine dyes display characteristic transient absorption (apparent absorption maximum at 580 nm) that decays in a nanosecond time scale and according to Schuster it can be attributed to mono-*cis* excited isomer [36]. On the other hand, Serpone et al. for dithiacarbocyanine dyes assigned this transient to the triplet excited state of the dye [31]. However, it is necessary to emphasize that the heavy atom effect creates a transient with apparent absorption maximum recorded at 620 nm and that the triplet energy transfer sensitization of dithiacarbocyanine also gives an absorption band with a maximum at 630 nm [36]. These observations allow us to anticipate that the non-emitting state exhibiting transient absorption band in the range 480–580 nm can be assigned to the absorption related to the presence of the excited mono-*cis* isomer.

The occurrence of the electron transfer between cyanine and borate ions leads to a quenching and a simultaneous shortening of the fluorescence lifetime of cyanine chromophore. Under the assumption that the electron transfer is the only additional quenching route available in the ion-pair (lifetime τ_{CyB}) compared with the parent dye (lifetime τ_{CyX}) the rate of the electron transfer for ion pair can be obtained from the Eq. (3):

$$k_{el} = \frac{1}{\tau_{CyB}} - \frac{1}{\tau_{CyX}} \quad (3)$$

The calculated rate constants are listed in Table 5.

The examination of the fluorescence lifetime of the tested cyanine borate salts shows a distinct shortening of the fluorescence lifetime of cyanine dye. This observation can be explained assuming the presence of an electron transfer reaction between the excited singlet state of the dye and the borate anion. The rate constants obtained from the fluorescence quenching experiment can be assigned to the intra-ion-pair electron transfer from the borate to the excited cyanine (k_{et}).

Table 5

The rate constants for electron transfer process in cyanine borates tested

Dye	k_{el} [s ⁻¹] CyB2	k_{el} [s ⁻¹] CyB3	k_{el} [s ⁻¹] CyB4	k_{el} [s ⁻¹]
Cy3	9.84E+08	1.48E+09	5.27E+08	1.07E+09
Cy4	1.55E+10		2.23E+08	9.97E08
Cy50			1.34E+10	
Cy8	4.21E+08	4.39E+08	1.1E+10	
Cy56	1.97E+10		1.41E+08	3.33E+08
Cy9	4.26E+08	1.03E+09	1.6E+10	2E+08
Cy47	6.5E+09			1.59E+10
Cy10	6.31E+08	6.33E+08	6.09E+09	
Cy11	2.06E+10			1.09E+09
Cy33		3.67E+09	1.05E+11	4.7E+09
Cy36	1.4E+10	1.55E+08		
Cy58	3.9E+08	2.93E+09	1.44E+09	2.84E+09
Cy59	6.57E+10	2.05E+09	6.85E+09	3.63E+09
Cy60	4.77E+10			2.83E+09
Cy63				2.35E+09
Cy65			1.6E+08	
Cy66		5.31E+09		8.97E+09
Cy64	5.45E+09	1.41E+09	4.34E+09	1.45E+09
Cy19	7.59E+09			
Cy41	1.27E+10	9.38E+09		4.62E+09
Cy45		5.18E+09		1.16E+11
Cy22	9.22E+09	1.86E+08		
Cy48	1.28E+09	4.56E+09		
Cy23	6.38E+08	1.09E+09	37686765	2.12E+09
Cy24	6.31E+09	1.05E+09	3.94E+08	
Cy27	4.48E+09	2.55E+08	2.02E+09	2.83E+08
Cy25		5.49E+09	2.83E+08	3.7E+09
Cy52		1.22E+09	5.94E+09	1.91E+08
Cy28				1.54E+09

The analysis of these data shows that the rate constants for the electron transfer process is ranging from 1.9×10^8 to $1.6 \times 10^{11} \text{ s}^{-1}$. These values are less than the rate constant for the electron transfer process for borate salts of *N,N'*-dimethylindocarbocyanine dyes in benzene solution (about 10^{13} s^{-1}) [7]. The introduction of the methyl or ethyl group to the polymethine chain causes an increase of the rate constant for the electron transfer process by about two orders of magnitude in many cases.

The main question arising during the quenching experiments is whether the fluorescing state of the cyanine is the state that is quenched and reduced by the borate. It is well known that the rate constants for the electron transfer can be related to the free energy for the electron transfer process through the classical Marcus equation, Eq. (4) where λ is the reorganization energy [7], and ΔG_{el} is described by Rehm–Weller Eq. (5).

$$\Delta G_{\text{el}}^{\#} = \frac{\lambda}{4} \left(1 + \frac{\Delta G_{\text{el}}^0}{\lambda} \right)^2 \quad (4)$$

$$\Delta G_{\text{el}} = E_{\text{ox}}(\text{D}/\text{D}^{\bullet+}) - E_{\text{red}}(\text{A}^{\bullet}/\text{A}) - Ze^2/\epsilon a - E_{00} \quad (5)$$

where: $E_{\text{ox}}(\text{D}/\text{D}^{\bullet+})$ is the oxidation potential of the electron donor, $E_{\text{red}}(\text{A}^{\bullet}/\text{A})$ is the reduction potential of the electron acceptor, E_{00} is the energy of the cyanine excited state and $Ze^2/\epsilon a$ is the Coulombic energy gained by bringing the radical ions to an encounter distance in a solvent with relative permittivity ϵ .

A plot of the data for the electron transfer process in cyanine borates according to this approach is shown in Figs. 4 and 5. The data presented in

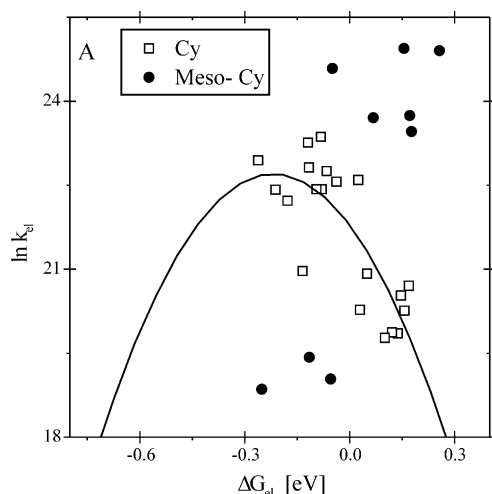


Fig. 4. The dependence of the rate of electron transfer on free energy for transfer of an electron from *n*-butyldiphenyl borate ion to the cyanine dyes tested.

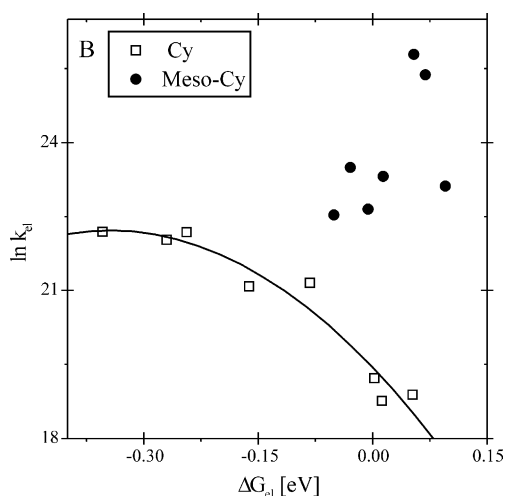


Fig. 5. The dependence of the rate of electron transfer on free energy for transfer of an electron from *tert*-butyldiphenyl borate ion to the cyanine dyes tested.

Figs. 4 and 5 behave as predicted by the theory of the electron transfer and allows to come to the conclusion that the state, which is quenched, is the fluorescing state. It should be noted that the points characterizing dyes are dispersed and more likely indicate the trend of the relationship than the superior fit to the Marcus theory. We believe that the high scattering of the experimental points

is related with the properties of cyanine borates, namely with the dissociate in character oxidation of borate anion.

4. Conclusion

Two different groups of symmetrical cyanine dyes, possessing, either the benzothiazole or bezoxazole ring were synthesized and their fluorescence lifetimes have been measured, by pico/femtosecond spectrometry. As obtained results show, for cyanine dyes bi-exponential decay of fluorescence was observed, while for cyanine with a substituent at the *meso* position, for the majority of dyes, mono-exponential decays were obtained. Based on the fluorescence measurements the rate of electron transfer process between excited dyes and borate anions was calculated and a short discussion on photophysics of cyanine dyes is given. The most important conclusion that arrived from the theoretical and experimental data is that the relationship between the rate of the electron transfer and the free energy for this reaction display typical “normal Marcus region” kinetic behavior only in group of dyes not substituted in the *meso* position.

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