Available online at www.sciencedirect.com

SCIENCE DIRECT®

Spectrochimica Acta Part A 62 (2005) 115–125

SPECTROCHIMICA
ACTA
PART A

www.elsevier.com/locate/saa

The synthesis and the solvent and substituent effect on the spectroscopic characteristic of 3-ethyl-2-(*p*-substitued styryl)benzothiazolium iodides

Janina Kabatc*, Beata Jędrzejewska, Piotr Orliński, Jerzy Pączkowski*

University of Technology and Agriculture, Faculty of Chemical Technology and Engineering, Seminaryjna 3, 85-326 Bydgoszcz, Poland

Received 20 October 2004; received in revised form 8 December 2004; accepted 10 December 2004

Abstract

The photophysical and photochemical properties of *p*-substitued 2-styryl-ethylbenzothiazolium iodides, possessing different electron-withdrawing or electron-donating groups are described. The dyes were prepared by the condensation of 3-ethyl-2-methylbenzothiazole salts with *p*-substituted benzaldehydes. The synthesis of suitable substrates is presented as well. We describe here the absorption, emission spectra and the luminescence quantum yield of hemicyanine dyes (SH) measured in 11 different organic solvents of varying polarity. Molecular structure of the synthesized dyes was established by ^{1}H NMR, electronic absorption and fluorescence spectrometry. The spectral data confirmed that all the compounds exist in E-configuration of their styryl residues. The planar molecular conformation is typical for the compounds with five-membered side aromatic moieties (for example benzothiazole). The compounds possessing N-alkyl substituent in phenyl ring, in contrast to the compounds with other substituents, exhibit low fluorescence quantum yield in THF solution. This indicates that for N-alkyl derivatives the non-radiative processes are much more effective than the radiative ones. The electronic absorption and fluorescence emission spectra of tested dyes demonstrate high sensitivity to the nature of substituent introduced into the aromatic ring.

Keywords: Hemicyanine dyes; Benzothiazole derivatives; Synthesis; Spectroscopic properties; Stokes shift

1. Introduction

A lot of classes of fluorescent organic dyes have found their successful application in science and technology. The best known, among them, are xanthenes, coumarins, naphtalimides, cyanines, various aryl-azoles, acridines and phenoazines [1].

Synthesis of new organic molecules and characterization of their photophysical molecular properties in different environments (pure solvents and molecular assemblies) are necessary prerequisites for further research in modern technologies.

Conjugated organic dye molecules are recognized to be important materials having novel, promising, electronic and photonic properties suitable for many technological applications.

The presence of heteroatom (nitrogen, oxygen or sulphur) in above-mentioned molecules usually does not reduce the brightness of their fluorescence, but brings considerable effect onto other optical characteristics: for example, molar extinction coefficient and band position in the absorption and fluorescence spectra. The changes in optical properties of the organic molecules upon their chemical modification can be foreseen by quantum-chemical simulations. However, the fluorescence quantum yield is a poorly predictable parameter for most organic molecules. For this reason, the experimental discovery of new class of fluorescent compounds retains its importance up to the present [1]. The *p*-substitued styrylbenzothiazole dyes with electron donor–acceptor moieties on opposite sides of styryl bond are particularly attractive for their spectral sensitivity towards local host environment and optical and electronic properties. When the

---

* Corresponding authors. Tel.: +48 52 3749045; fax: +48 52 3749009.
E-mail addresses: nina@atr.bydgoszcz.pl (J. Kabatc), paczek@atr.bydgoszcz.pl (J. Pączkowski).

1386-1425/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2004.12.014

two ends are different, the molecules can have a permanent electric dipole and show non-linear optical behavior.

Polymethine dyes are moderately fluorescent and they absorb and emit light mostly in the visible region of the optical spectrum which is a function of the chain length and a structure of the terminating moieties. It is known that an elongation of the polymethine chain increases the fluorescence quantum yields, but, as it grows further, it causes a decrease of the fluorescence efficiency [2]. The knowledge of the fluorescence quantum efficiencies of organic molecules in solution is fundamental in many important applications in physical chemistry and photonics [3].

A number of styryl dyes (styrene-like dyes with different aromatic groups on opposite sides of styryl double bond) have been synthesized and investigated [3–6]. Our main task, in the present work, was the synthesis and the study of the chemical structure and fluorescence properties of the 18 representatives of the 3-ethyl-2-(*p*-substitued styryl) benzothiazolium iodides, that differ by their electron donor properties of substituent present in the aromatic moiety. In this paper, we report the photophysical properties of the group of fluorescent benzothiazole based styryl dyes, called hemicyanine dyes, in organic solvents.

2. Experimental

2.1. Materials

2-Methylbenzothiazole, Rhodamine B, Coumarin I, ethyl iodide, *p*-substitued benzaldehydes and solvents were obtained from Aldrich. Aldehydes, as substrates for synthesis of SH3–SH11 dyes were synthesized according to the procedure given by Gawinecki et al. [7].

3-Ethyl-2-(*p*-substitued styryl)benzothiazolium iodides were synthesized in our laboratory using procedure described in a previous report [8].

2.2. Synthesis

A general route for the synthesis of the prepared hemicyanine dyes is shown in Scheme 1.

2.2.1. 3-Ethyl-2-methylbenzothiazole iodide

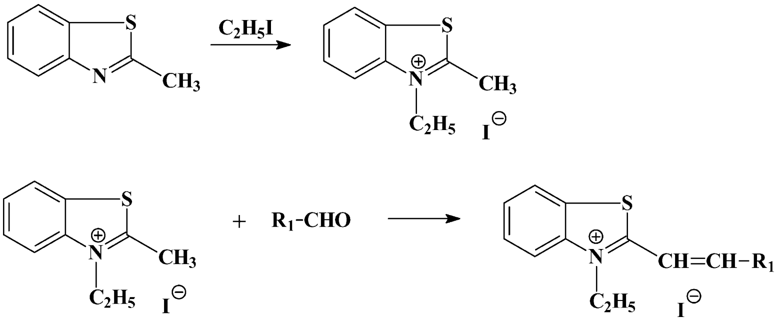
3-Ethyl-2-methylbenzothiazole iodide was prepared by Hamer's method [8]. The mixture of 2-methylbenzothiazole (1 mmol) and ethyl iodide (1.2 mmol) was heated at 100 °C for 40 h. After the extraction with dry ether, the crude product was recrystalized from absolute ethanol, washed with ether and dried (yield 70%).

2.2.2. 3-Ethyl-2-(p-substitued styryl)benzothiazolium iodides

A mixture of 3-ethyl-2-methylbenzothiazole iodide (1 mmol), *p*-substitued benzaldehyde (1 mmol) and acetic anhydride (20 ml) was refluxed for 20 min, than poured into a warm solution of potassium iodide (4 mmol) in water (20 ml). The precipitated product was filtered, washed with water and recrystallized from methanol.

2.3. Measurements

For the measurements of absorption and emission spectra and fluorescence quantum yield (Φ) the 1.0×10^{-5} M SH solutions in various solvents were presented. At such concentration no aggregation or self-absorption effects of the dyes were observed [9]. Absorption spectra were recorded at room temperature using a Varian Cary 3E spectrophotometer, and fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorimeter. Absorption and emission spectra were recorded with a spectroscopic quality: acetonitrile (MeCN), acetone, chloroform, dimethylformamide (DMF), dimethylsulfoxide (DMSO), dichloromethane, 1,2-dichloroethane, tetrahydrofuran (THF) and ethyl acetate (EtOAc). The fluorescence measurements were performed at an ambient temperature.The fluorescence quantum yields for the dyes in ethanol were determined as follows. The fluorescence spectrum of a dilute (<25 μM) dye solution was recorded by excitation at the absorption band maximum of the standard. A dilute Rhodamine B in ethanol ($\Phi = 0.55$ [10]) was used as reference for dyes SH1–SH11. The fluorescence spectrum of Rhodamine B was obtained by excitation at its absorption peak at 530 nm. Whereas the fluorescence quantum yields of SH12–SH21 dyes were determined by comparing with Coumarin I fluorescence in ethanol which has been shown to have a quantum yield of 0.64 [11]. In this case the solutions



Scheme 1.

of tested dyes have absorbances around 0.1 at the excitation wavelength (418 nm). The quantum yield of the tested dye (Φ_{dye}) was calculated using the equation

$$\Phi_{\text{dye}} = \Phi_{\text{ref}} \frac{I_{\text{dye}} A_{\text{ref}}}{I_{\text{ref}} A_{\text{dye}}} \tag{1}$$

where Φ_{ref} is the fluorescence quantum yield of reference (Rhodamine B or Coumarin I) in ethanol, A_{dye} and A_{ref} are the absorbances of the dye and reference samples at their excitation wavelengths, I_{dye} and I_{ref} are the areas arbitrary units of the corrected fluorescence spectra (plotted in frequency scale) for the dyes and reference samples, respectively (integrated areas of fluorescence spectrum).

The ^{1}H NMR spectra were recorded with the use of a Varian spectrometer Gemini 200 operating at 200 MHz. Dimethylsulfoxide (DMSO) was used as the solvent and tetramethylsilane (TMS) as internal standard.

Melting points (uncorrected) were determined on the Boëthius apparatus.

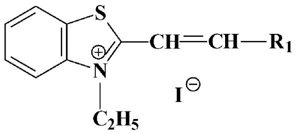
The reduction potentials of hemicyanine dyes were measured by cyclic voltammetry. An electroanalitycal MTM system model EA9C-4z (Cracow, Poland), equipped with a small volume cell, was used for the measurements. A 1 mm platinum disc electrode was used as the working electrode, a Pt wire constituted the counter electrode and an Ag–AgCl electrode served as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile.

3. Results and discussion

The structures of the 18 styryl benzothiazole (SH) dyes synthesized (Scheme 2) have one type of electron acceptor group (benzothiazole) but differ in a structure of phenyl moiety substituent.

The hemicyanine iodides SH were synthesized by a two-step reaction (Scheme 1).

The alkylation of the nitrogen atom of 2-methylbenzothiazole was the first step of synthesis. Next, the 3-ethyl-2-methylbenzothiazolium iodide was condensed with *p*-substitued benzaldehyde via Knoevenagel reaction using pyridine or piperidine as the catalyst. The condensation for the entire series of *N*-alkyl substitued 2-methylbenzothiazole with 18 different benzaldehydes was performed. The yield of the reaction varied in the range of 20–84%. To our best knowledge, the majority of the synthesized compounds have not been described in literature, yet.



Scheme 2.

The structure and purity of the prepared compounds were confirmed by NMR spectroscopy and thin layer chromatography.

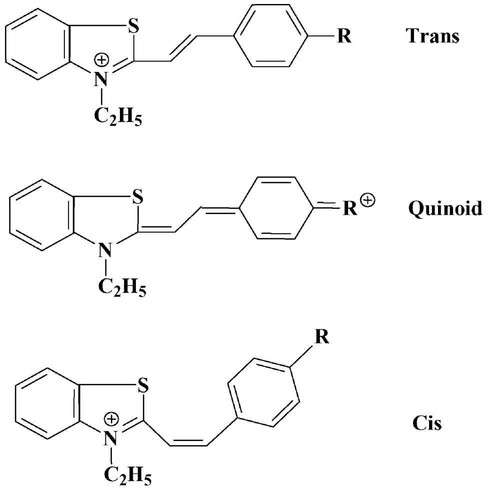
The ^{1}H NMR spectra are in good accordance with the chemical structure expected for synthesized dyes (Table 1).

It is noteworthy that the ^{1}H NMR spectra display two characteristic doublets localized at chemical shifts about 7 and 8 ppm. They are attributed to both vinyl hydrogen atoms. The coupling between these protons ($J \approx 15$ Hz), indicates the *trans* form of the ground state of all synthesized compounds. There is no evidence for the formation of the *cis*-structure, probably because of steric hindrance caused by the aromatic groups [12]. The 3-ethyl-2-methylbenzothiazolium iodide is a grey-color powder, whereas the hemicyanines are intensely yellow–orange–red. All the samples obtained, according to thin-layer chromatography (silica gel 60, F-254), with the use of methanol–acetone mixtures (2:1) as eluent, were pure.

Benzothiazole based styryl dyes studied display several specific properties that are similar to other styryl dyes reported in literature [3–6]. All styryl dyes tested in this study are charged and have a common structural feature, namely, possess an electron donor and electron acceptor moiety located on opposite sides of a styryl double bond. As the NMR spectra have shown, the tested styryl dyes in the ground state exist as *trans* isomer.

An important problem, to be addressed interpreting the fluorescence spectroscopic behavior in organic solvents, is the identification of the structure or structures of the dye in various solvents. Fluorescing molecules with rigid ring structures (like anthracene) retain the same structure in ground and excited state in any organic solvent. Fluorescing molecules of type studied in this work possess the possibility of two isomeric structures because of the flexibility about the styryl bond.

Scheme 3 shows possible structures of the dyes under the study.



Scheme 3.

Table 1
Characteristic of 3-ethyl-2-(*p*-substituted styryl)benzothiazolium iodides

Dye	Melting point (°C)	Molecular formula	Positions of signals ^{1}H-NMR spectra, σ (ppm) and coupling constants *J* (Hz)
SH 1	226	$C_{26}H_{28}N_2O_3S_2$	1.392–1.462 (3H,CH_3); 2.281 (3H, CH_3); 3.114(6H, CH_3); 4.815–4.851 (2H, N—CH_2); 7.585–7.662 (*J* = 15.4 Hz, 1H); 8.055–8.13 (*J* = 15 Hz, 1H); 6.824–6.867 (2H); 7.085–7.126 (2H); 7.451–7.491 (2H); 7.676–7.788 (2H); 7.911–7.956 (2H); 8.158–8.322 (2H)
SH 2	232	$C_{21}H_{25}IN_2S$	1.049–1.190 (6H, CH_3); 1.382–1.45 (3H, CH_3); 3.405–3.522 (4H, CH_2); 4.805–4.840 (2H, CH_2); 6.796–6.842 (2H); 7.535–7.610 (*J* = 15 Hz, 1H); 8.023–8.100 (*J* = 15.4 Hz, 1H); 7.660–7.770 (2H); 7.776–7.931 (2H); 8.141–8.308 (2H)
SH 4	121	$C_{25}H_{33}ISN_2$	0.896–0.968 (6H, CH_3); 1.298–1.418 (8H, CH_2); 1.452–1.554 (3H, CH_3); 3.408–3.482 (4H, CH_2); 4.798–4.834 (2H, N—CH_2);7.535–7.610 (J=15 Hz, 1H); 8.032–8.107 (*J* = 15 Hz, 1H); 6.785–6.830 (2H); 7.629–7.815 (1H); 7.882–7.925 (2H); 8.145–8.312 (2H)
SH 7	230	$C_{21}H_{23}IN_2S$	1.401–1.473 (3H, CH_3); 2.481–2.571 (4H, CH_2); 3.077 (4H, N-CH_2); 4.740–4.836 (2H, N—CH_2); 7.702–7.777 (*J* = 15 Hz, 1H);8.031–8.105 (*J* = 14.8 Hz, 1H); 6.808–6.853 (2H); 7.111–7.189 (1H); 7.540–7.686 (1H); 7.833–7.933 (1H); 8.137–8.214 (2H); 8.275–8.324 (1H)
SH 8	238	$C_{22}H_{25}IN_2S$	1.393–1.463 (3H, CH_3); 1.626 (6H, CH_2); 3.510 (4H, CH_2); 4.798–4.868 (2H, N—CH_2); 7.613–7.690 (*J* = 15.4 Hz, 1H); 8.046–8.123 (*J* = 15.4 Hz, 1H); 7.035–7.078 (2H); 7.653–7.831 (2H);7.944–8.899 (2H); 8.14–8.337 (2H)
SH 9	241	$C_{20}H_{21}IN_2S$	1.373–1.442 (3H, CH_3); 2.956 (4H, N—CH_2); 3.027–3.111 (4H, CH_2); 3.620–3.703 (3H, CH_3); 4.766–4802 (2H, N—CH_2); 7.467–7.543 (*J* = 15.2 Hz, 1H); 7.966–8.042 (*J* = 15.2 Hz, 1H); 6.564–6.607 (1H); 7.641–7.852 (4H); 8.063–8.287 (2H)
SH 10	236	$C_{21}H_{23}IN_2S$	1.384–1.452 (3H, CH_3); 1.909 (2H, CH_2); 2.735–2.795 (2H, CH_2); 3.056 (3H, CH_3); 3.417–3.471 (2H, CH_2); 4.785–4.822 (2H, CH_2); 7.615–7.692 (*J* = 15.4 Hz, 1H); 7.969–7.8.044 (*J* = 15 Hz, 1H); 6.686–6.674 (1H); 7.653–7.805 (4H); 8.081–8.297 (2H)
SH 11	230	$C_{23}H_{25}IN_2S$	1.369–1.439 (3H, CH_3); 1.904–1.921 (4H, CH_2); 2.508–2.764 (4H, CH_2); 3.379–3.407 (4H, N—CH_2); 4.745–4.781 (2H, N—CH_2) 7.396-7.471 (J=15 Hz, 1H); 7.867–7.941 (*J* = 14.8 Hz, 1H); 7.523 (2H); 7.621–7.739 (2H);8.034–8.263 (2H)
SH 12	251	$C_{25}H_{25}NO_3S_2$	1.433–1.504 (3H, CH_3); 2.281–2.410 (3H, CH_3);2.490–2.508 (3H, CH_3); 4.919–5.017 (2H, N—CH_2); 7.457–7.378 (*J* = 15.8 Hz, 1H); 7.961–8.040 (*J* = 15.8 Hz, 1H); 7.086–7.126 (2H); 7.420–7.487 (2H); 7.584–7.658 (1H); 7.760–7.920 (2H); 7.974–8.015 (2H); 8.197 (1H); 8.276–8.468 (2H)
SH 13	239	$C_{26}H_{27}NO_3S_2$	1.186–1.262 (3H, CH_3); 1.433–1.504 (3H, CH_3); 2.280 (2H, CH_2); 2.649–2.762 (3H, CH_3); 4.957–4.993 (2H, N—CH_2); 7.405–7.479 (*J* = 14.8 Hz, 1H); 7.920–7.994 (*J* = 14.8 Hz, 1H); 7.083–7.126 (1H); 7.447–7.488 (2H); 7.761–7.884 (2H); 7.928–7.965 (1H); 8.036–8.044 (2H); 8.205–8.330 (2H); 8.423–8.469 (1H)
SH 14	248	$C_{30}H_{27}NO_3S_2$	1.459–1.531 (3H, CH_3); 2.280 (3H, CH_3); 4.991–.027 (2H, N—H_2); 7.806–7.866 (*J* = 12 Hz, 1H); 8.214–8.280 (*J* = 13.2 Hz, 1H); 7.082–7.124 (2H); 7.451–7.577 (4H); 7.847–8.067 (6H); 8.146–8.172 (2H); 8.309–8.357 (2H); 8.443–8.488 (1H)
SH 15	239	$C_{25}H_{24}NO_4S_2$	1.425–1.495 (3H, CH_3); 2.276 (3H, CH_3); 3.881 (3H, CH_3); 4.925–4.961 (2H, N—CH_2); 7.078–7.155 (*J* = 15.4 Hz, 1H); 7.733–7.803 (*J* = 15.4 Hz, 1H); 7.082–7.120 (4H); 7.455–7.495 (1H); 7.765–7.932 (2H); 8.056–8.100 (1H); 8.181–8.296 (2H); 8.391–8.438 (2 H)
SH 16	258	$C_{26}H_{26}NO_4S_2$	1.335–1.492 (6H, CH_3); 2.280 (3H, CH_3); 4.147–4.18 (2H, O—CH_2); 4.920–4.956 (2H, N—CH_2); 7.827–7.924 (*J* = 15.6 Hz, 1H); 8.181–8.258 (1H); 7.086–7.488 (1H); 7.769–7.819 (1H); 7.846–8.088 (1H); 8.291–8.390 (1H)
SH 17	204	$C_{17}H_{16}INOS$	1.413–1.483 (3H, CH_3); 4.889–4.925 (2H, N—H_2); 6.948–6.910 (1H); 7.711–7.786 (*J* = 15 Hz, 1H); 7.949–8.126 (*J* = 15.4 Hz, 1H); 7.748–7.882 (2H); 7.786–7.846 (2H); 7.822–7.882 (1H); 8.222–8.263 (1H); 8.410–8.370 (1H); 10.623 (1H)
SH 18	241	$C_{17}H_{15}INFS$	1.435–1.507 (3H, CH_3); 4.957–4.993 (2H, N—CH_2); 7.896–7.973 (*J* = 15.4 Hz, 1H); 8.231–8.309 (*J* = 15.6 Hz, 1H); 7.397–7.486 (2H); 7.802–7.858 (2H); 8.052–8.215 (2H); 8.341–8.480 (2H)
SH 19	257	$C_{17}H_{15}INBrS$	1.445–1.517 (3H, CH_3); 4.696–5.005 (2H, N—CH_2); 7.781–7.859 (*J* = 15.6 Hz, 1H); 8.049–8.128 (*J* = 15.8. 1H); 7.824–8.065 (4H); 8.128–8.211 (2H); 8.291–8.494 (2H)
SH 20	273	$C_{17}H_{15}IN_2O_2S$	1.468–1.538 (3H, CH_3); 4.989–5.060 (2H, N—CH_2); 7.900–7.977 (*J* = 15.4 Hz, 1H); 8.422–8.497 (*J* = 15 Hz, 1H); 7.815–7.970 (1H); 8.505–8.544 (1H); 8.288–8.399 (6H)
SH 21	254	$C_{19}H_{18}INOS$	1.456–1.527 (3H, CH_3); 2.323 (3H, CH_3); 4.973–5.011 (2H, N—CH_2); 7.984–8.073 (*J* = 15.8 Hz, 1H); 8.239–8.316 (*J* = 15.4 Hz, 1H); 7.334–7.387 (2H); 7.814–7.866 (1H); 8.073 (1H); 8.130–8.173 (2H); 8.353–8.486 (2H)

The spectra were measured in DMSO-d 6 with TMS as internal standard at 25 °C.

It should be emphasized that the *quinoid* structure might also be considered as intramolecular charge transfer (ICT) state. In principle the *trans* and *quinoid* structures can be treated as mesomeric resonance structures, with the positive charge localized on different atoms, on the benzothiazole nitrogen in the case of *trans* isomer and on the nitrogen atom of the substituent of styryl moiety for *quinoid* form [13]. This is possible only for SH1–SH11 dyes. For this group of molecules, solvents may interact differently with the two isomers making possible the presence of either *trans* or *quinoid* or both forms. Situation is less complex for SH12–SH21 dyes. Here, there is no possibility of the formation of *quinoidal* structure of the dye. However, it is difficult to predict the role of a solvent in stabilization of excited states for this group of the dyes. Therefore, one has to collect experimental spectroscopic data in a variety of organic solvents to identify multiple structures of the dye in the ground and excited states.

The main physicochemical data for the compounds under the study are collected in Tables 2 and 3 .

The SH dyes absorb strongly in the visible region and are characterized by a molar absorption coefficient of about $3 \times 10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, which is in good agreement with those given in the literature for other similar type of the dyes [14]. The high value of the molar absorption coefficient indicates an extensive conjugation of π-electrons suggesting a planar structure of the dye molecule in its ground state.

The absorption and fluorescence emission spectra of SH1–SH16 were measured in several organic solvents (1,4-dioxane, benzene, chloroform, ethyl acetate, tetrahydrofuran THF, 1,2-dichloromethane, 1,2-dichloroethane, acetone, acetonitrile, *N*,*N*-dimethylformamide DMF, dimethylsulfoxide DMSO). The normalized absorption and emission spectra of two selected dyes, in three different solvents, are presented in Figs. 1 and 2 for illustration.

The absorption and emission spectra of SHs are affected by the organic solvents. In general, there is a blue shift observed in absorption maxima of SHs tested with increasing polarity of the solvent (Table 3). The compounds we study are ionic dyes which exhibit a polar character in the ground state. The solvent molecules are oriented in such a way as required by the polar character of the host molecule. During the transition, which occurs within a very small time interval, only the electrons have the time to change position. The excited molecules, in which the electric dipole has been weakened and has been reoriented, are now within a solvent cage that is no longer adopted to the electronic requirements of the excited molecule, since the solvent cage is suitable for the electronic distribution in the ground state molecule. Thus, a polar solvent creates a stabilizing solvent cage around these ionic dyes in the ground state, but a destabilizing solvent cage for the excited state. The transition energy increases with increasing solvent polarity. An increase in solvent polarity results in hypsochromic shift of the charge transfer band, i.e. to shorter wavelengths.

The fluorescence emission spectra band are somewhat narrower than the absorption spectra (see Table 3 and Figs. 1 and 2). If the broadening of the spectra is understood as deriving from the population of the thermally available conformers, then according to Rettig and coworkers [15], the observed results can be taken as the evidence that some of these conformers are non-emissive (demonstrated by a reduction of fluorescence band width). The twisting around the molecule bonds gives this type of a conformer. In the case of the twist of the olefinic double bond the obtained isomer should be deactivated mainly by radiationless processes because the energy gap between its excited state and the ground state is very small [15].

The absorption and emission spectra of SH dyes are sensitive to the solvent which is attributed to the difference in the dipole moment in the ground and excited states. The spectra showed considerable spectral shifts in applied organic solvents. The difference in energy between the absorbed and emitted radiation is known as the Stokes shift [1]. Stokes shift ($\nu_{\mathrm{ab}} - \nu_{\mathrm{fl}}$), is one of the quantitative parameters which is useful to understand the origin of the variation of spectral shift in organic solvents.

The Lippert equation is a simple and the most widely used expression to explain the general solvent effects (due to the dielectric constant (ε) and the refractive index (n) of the solvent). The Stokes shift is dependent on the orientational polarizability of a solvent (Δf), which is linearly related to this. The Stokes shift values obtained for hemicyanine dyes tested are also given in Table 3. The highest value of Stokes shift (>2200 up to 7000 cm^{-1}) was observed in acetonitrile, DMF and DMSO, and the lowest (1000–1600 cm^{-1}) in dichloromethane.

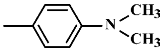
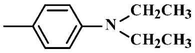
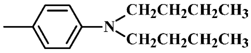
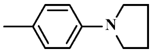
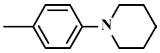
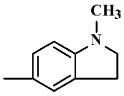
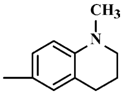
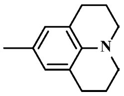
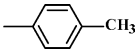
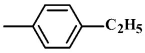
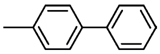
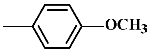
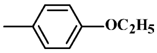
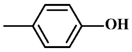
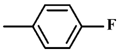
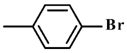
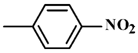
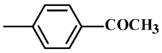
It is clearly visible that dyes possessing strong electron donor substituents such as *N*,*N*-dialkylamino groups have smaller Stokes shift than those possessing weak electron-donor groups or strong electron acceptor groups. In this case the Stokes shift varies in the range from 3000 to 7000 cm^{-1}. A typical magnitude of Stokes shift in some symmetrical cyanines, due to a change in dipole moments, varies in the range of 2500–5000 cm^{-1} [14].

The application of the Lippert and Mataga theory helps to understand better the observed properties [13]. According to this theory, the specific solvent effects can be expressed by two equations. Eq. (2) describes the behavior of the absorption band by the following expression:

$$hc\bar{\nu}_{\mathrm{ab}}^{\mathrm{CT}} \cong hc\bar{\nu}_{\mathrm{ab}}^{\mathrm{vac}} - \frac{2\vec{\mu}_{\mathrm{g}}(\vec{\mu}_{\mathrm{e}} - \vec{\mu}_{\mathrm{g}})}{a_0^3}\left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2}\frac{n^2 - 1}{2n^2 + 1}\right] \qquad (2)$$

where $hc\bar{\nu}_{\mathrm{ab}}^{\mathrm{CT}}$ and $hc\bar{\nu}_{\mathrm{ab}}^{\mathrm{vac}}$ are the energies related to the spectral position of the CT absorption maxima in solution and to the value extrapolated to the gas-phase respectively; $\vec{\mu}_{\mathrm{g}}$ and $\vec{\mu}_{\mathrm{e}}$ are the dipole moments of the solute in the ground and excited state; a_0 is the effective radius of the Onsager's cavity [16], ε is the static dielectric constant, and n is the refractive index of the solvent.

Table 2
Data of absorption, fluorescence spectra and electrochemical properties of tested dyes

Dye	R_1	Absorption		Fluorescence		E^0 (red) (V)	E^0 (ox) (V)
		λ (nm)	ε ($M^{-1}\,cm^{-1}$)	λ (nm)	Φ (±0.1)		
SH 1		521	30600	597	0.015	−0.97	0.61
SH 2		536	21400	597	0.009	−1.00	0.65
SH 4		538	15600	601	0.013	−0.90	–
SH 7		535	41800	600	0.006	−1.07	–
SH 8		527	35700	603	0.008	−0.75	1.01
SH 9		554	34800	611	0.003	−0.92	–
SH 10		549	46300	606	0.004	−0.98	–
SH 11		569	66000	620	0.005	−1.08	–
SH 12		388	22400	515	0.226	−0.99	–
SH 13		388	31500	480	0.172	−1.02	–
SH 14		403	34600	514	0.726	−1.00	–
SH 15		413	37700	507	0.322	−1.11	–
SH 16		416	31900	510	0.160	−0.90	0.98
SH 17		426, 554	24400	574	0.086	−1.03	–
SH 18		376	36000	470	0.125	−0.93	0.63
SH 19		381	26300	473	0.131	−1.07	0.92
SH 20		370	11000	–	0.116	−0.94	–
SH 21		382	24400	472	0.184	−0.97	–

The presented data were recorded in ethyl acetate solution. The fluorescence quantum yield was determined in THF solution.

The second equation describes the solvatochromic effect on the spectral position of the CT fluorescence spectra band and is given by:

$$hc\bar{\nu}_{\mathrm{fl}}^{\mathrm{CT}} \cong hc\bar{\nu}_{\mathrm{fl}}^{\mathrm{vac}} - \frac{2\vec{\mu}_{\mathrm{e}}(\vec{\mu}_{\mathrm{e}} - \vec{\mu}_{\mathrm{g}})}{a_0^3}\left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2}\frac{n^2 - 1}{2n^2 + 1}\right] \tag{3}$$

where $hc\bar{\nu}_{\mathrm{fl}}^{\mathrm{CT}}$ and $hc\bar{\nu}_{\mathrm{fl}}^{\mathrm{vac}}$ are the spectral positions of the solvent equilibrated CT fluorescence maxima and the value extrapolated to the gas-phase correspondingly. This type of treatment of solvent effect for selected dyes is shown in Fig. 3.

The analysis of the trends presented for SH2 and SH12 (Fig. 3) (similarly behave other dyes) allows to conclude that: (i) the negative value of $2\vec{\mu}_{\mathrm{g}}(\vec{\mu}_{\mathrm{e}} - \vec{\mu}_{\mathrm{g}})$ term suggests that $\vec{\mu}_{\mathrm{e}} < \vec{\mu}_{\mathrm{g}}$; (ii) the positive value of $2\vec{\mu}_{\mathrm{e}}(\vec{\mu}_{\mathrm{e}} - \vec{\mu}_{\mathrm{g}})$ term allows to conclude that for relaxing molecules $\vec{\mu}_{\mathrm{e}} > \vec{\mu}_{\mathrm{g}}$.

Combination of mentioned above relationships indicates the following possibilities: (i) the dipole moment of the ground state, form which molecule is excited, is different to that from which excited molecule relaxes; (ii) the emission occurs from the molecule with dipole moment different from that obtained after the Franck–Condon excitation; (iii) the emission occurs from the molecule characterized by the dipole moment different from that from which is excited.

It is known, that a linear dependence of Stokes shift and Δf (polarizability parameter [13]) for all solvents validates

Table 3
Steady state spectral properties of dyes SH solutions

Dye	Solvent	λ_{ab} (nm)	ε (M^{-1} cm^{-1})	λ_{fl} (nm)	$\Delta\nu$ (cm^{-1})	$FWHM_{ab}$ (cm^{-1})	$FWHM_{fl}$ (cm^{-1})
SH 1	1,4-Dioxane	529	48700	597	2150	2470	1240
	Benzene	533	43900	601	2120	2500	1270
	Chloroform	542	71200	592	1560	2100	1190
	Ethyl acetate	521	30600	597	2430	2590	1250
	THF	527	53600	600	2310	2480	1220
	Dichloromethane	549	86400	595	1410	1840	1110
	1,2-Dichloroetane	546	75000	598	1600	1950	1140
	Acetone	522	59100	598	2450	2490	1220
	Acetonitrile	522	62400	599	2450	2520	1240
	DMF	525	55100	606	2540	2570	1200
	DMSO	525	54600	609	2630	2630	1230
SH 2	1,4-Dioxane	542	16600	602	1830	2100	1020
	Benzene	555	43600	603	1440	1900	1000
	Chloroform	559	75200	598	1170	1660	1180
	Ethyl acetate	536	21400	597	1900	2050	1010
	THF	544	69100	601	1740	2160	1020
	Dichloromethane	557	84800	606	1460	1760	1110
	1,2-Dichloroetane	557	76600	601	1310	1640	1010
	Acetone	533	59300	607	2290	2310	1250
	Acetonitrile	530	58200	600	2280	2300	960
	DMF	532	54300	606	2280	2380	1070
	DMSO	535	53000	609	2280	2400	1090
SH 4	1,4-Dioxane	541	15600	602	1860	2010	1210
	Benzene	558	94500	605	1390	1910	1100
	Chloroform	561	103300	603	1240	2180	1060
	Ethyl acetate	538	15600	601	1950	2160	1140
	THF	545	13840	605	1820	2110	1100
	Dichloromethane	563	116400	605	1240	1660	1040
	1,2-Dichloroetane	560	104200	606	1350	1690	1070
	Acetone	536	81800	604	2100	2240	1100
	Acetonitrile	535	83800	603	2120	2230	1110
	DMF	536	75800	609	2230	2330	1140
	DMSO	537	72300	611	2260	2330	1170
SH 7	1,4-Dioxane	533	43600	597	2020	2270	1170
	Benzene	552	93700	603	1530	2420	880
	Chloroform	554	81000	598	1330	1800	1070
	Ethyl acetate	535	41800	600	2030	2310	950
	THF	541	42100	601	1850	2080	930
	Dichloromethane	558	95100	600	1270	1620	950
	1,2-Dichloroetane	555	86100	610	1620	1720	1020
	Acetone	531	62300	602	2210	2280	910
	Acetonitrile	531	66400	599	2130	2340	2060
	DMF	535	59000	605	2170	2390	970
	DMSO	536	54300	603	2060	2330	930
SH 8	1,4-Dioksan	538	35400	597	1830	3340	1170
	Benzene	545	34500	605	1820	4360	1230
	Chloroform	557	34600	601	1320	2010	1100
	Ethyl acetate	527	35700	603	2400	2730	1210
	THF	536	35200	608	2200	2260	1200
	Dichloromethane	555	34500	605	1500	2070	1150
	1,2-Dichloroetane	556	34500	605	1470	2080	1150
	Acetone	524	35700	605	2540	2770	1220
	Acetonitrile	522	35700	605	2620	2750	1220
	DMF	524	35400	610	2690	2910	1250
	DMSO	524	35400	613	2780	2920	1190
SH 9	1,4-Dioksan	563	14200	609	1330	1930	1150
	Benzene	571	115600	616	1280	2460	1140
	Chloroform	571	59000	610	1130	1700	1080
	Ethyl acetate	554	34800	611	1680	2340	1150
	THF	558	43000	615	1650	2240	1150

Table 3 (*Continued*)

Dye	Solvent	λ_{ab} (nm)	ε (M^{-1} cm^{-1})	λ_{fl} (nm)	$\Delta\nu$ (cm^{-1})	FWHM$_{ab}$ (cm^{-1})	FWHM$_{fl}$ (cm^{-1})
	Dichloromethane	573	70000	614	1160	1650	1070
	1,2-Dichloroetane	570	58000	612	1220	1670	1180
	Acetone	548	51400	613	1930	2320	1120
	Acetonitrile	546	46900	613	2000	2310	1120
	DMF	550	41000	618	1990	2470	1180
	DMSO	552	41200	623	2070	2440	1250
SH 10	1,4-Dioxane	556	12700	604	1420	1800	1160
	Benzene	569	86000	611	1210	1720	1100
	Chloroform	569	89800	606	1070	1590	1030
	Ethyl acetate	549	46300	606	1720	2230	1130
	THF	554	58200	611	1680	2140	1100
	Dichloromethane	569	108600	611	1220	1200	1020
	1,2-Dichloroetane	567	85800	611	1270	1680	1030
	Acetone	544	69900	611	2010	2270	1100
	Acetonitrile	543	69500	610	2030	2220	1090
	DMF	545	64700	616	2120	2340	1110
	DMSO	547	62400	619	2130	2390	1120
SH 11	1,4-Dioxane	577	30900	616	1100	1670	1160
	Benzene	584	154700	624	1090	1850	1080
	Chloroform	587	100500	621	930	1350	1000
	Ethyl acetate	569	66000	620	1440	1910	1090
	THF	573	34900	622	1370	1730	1060
	Dichloromethane	587	119900	625	1030	1310	970
	1,2-Dichloroetane	585	94100	622	1020	1450	1130
	Acetone	566	77400	622	1600	1910	1070
	Acetonitrile	565	76200	622	1630	1900	1050
	DMF	567	69800	626	1670	1980	1150
	DMSO	568	61200	629	1700	2030	1100
SH 12	1,4-Dioxane	392	18300	514	6060	3390	2930
	Benzene	395	27500	517	5960	3030	2980
	Chloroform	400	26500	517	5640	3200	2620
	Ethyl acetate	388	22400	515	6340	5870	2690
	THF	391	21400	519	6310	4540	2920
	Dichloromethane	402	28800	483	4180	3250	2170
	1,2-Dichloroetane	401	28700	523	5820	3190	2530
	Acetone	387	25500	523	6730	7250	2640
	Acetonitrile	387	10000	519	6560	8470	2760
	DMF	390	24100	524	6540	3530	2660
	DMSO	386	17200	527	6930	4360	2650
SH 13	1,4-Dioxane	392	26900	484	4840	3260	3340
	Benzene	391	33300	479	4700	3040	3610
	Chloroform	400	33800	514	5550	3100	2640
	Ethyl acetate	388	31500	480	4950	3350	3090
	THF	393	30300	480	4620	3200	3210
	Dichloromethane	403	31900	–	–	2970	–
	1,2-Dichloroetane	402	36700	489	4440	3100	3090
	Acetone	387	34500	479	4980	5950	3040
	Acetonitrile	381	17400	475	5210	6720	3580
	DMF	389	32800	483	5000	3250	3120
	DMSO	391	33300	482	4830	3290	3180
SH 14	1,4-Dioxane	408	29500	516	5140	3460	3160
	Benzene	416	147500	517	4690	3830	3020
	Chloroform	418	37400	513	4450	3400	2660
	Ethyl acetate	403	34600	514	5370	3520	2890
	THF	406	34400	518	5330	3330	2750
	Dichloromethane	421	41300	500	3760	3320	1160
	1,2-Dichloroetane	420	40300	525	4760	3370	2590
	Acetone	402	40500	520	5650	4560	2680
	Acetonitrile	393	16300	516	6080	8240	2960
	DMF	404	35900	524	5660	3420	2620
	DMSO	406	38800	525	5590	8490	2650

Table 3 (*Continued*)

Dye	Solvent	λ_{ab} (nm)	ε ($M^{-1}\,cm^{-1}$)	λ_{fl} (nm)	$\Delta\nu$ (cm^{-1})	$FWHM_{ab}$ (cm^{-1})	$FWHM_{fl}$ (cm^{-1})
SH 15	1,4-Dioxane	420	32400	512	4270	3390	2700
	Benzene	423	19000	511	4070	3250	2710
	Chloroform	429	37800	510	3690	3190	2970
	Ethyl acetate	413	37700	507	4490	3420	2580
	THF	419	34900	512	4320	3260	2480
	Dichloromethane	432	43700	521	3950	3100	2380
	1,2-Dichloroetane	430	42000	511	3690	3110	2420
	Acetone	414	40300	511	4590	3300	2440
	Acetonitrile	418	35000	507	4180	3230	3070
	DMF	414	39300	514	4690	3350	2430
	DMSO	416	37800	514	4580	3310	2420

$\Delta\nu$ – Stokes shift, $FWHM_{ab}$ – absorption full width at half maximum, $FWHM_{fl}$ – fluorescence full width at half maximum.

the Lippert–Mataga equation and confirms that the dye has a single structure in the ground and excited states and the slope depends upon the change in dipole moment upon excitation [13]. This correlation predicts also that the Stokes shift should linearly increase with the orientational polarizability. In all tested dyes a linear correlation, with good coefficient fit, between Stokes shift and Δf was observed for all solvents used with expection of the halogenated solvents. The most important deviation of the spectroscopic result is observed in chloroform, dichloromethane and 1,2-dichloroethane. In above-mentioned solvents the Stokes shift is very low when compared to the solvents of similar polarity and viscosity. The experimental results strongly suggest that there is a specific interaction between SH dye and halogenated solvents. The nature of this interaction and the structure of the dye–solvent complex are not clear at present. Similar results were obtained for styrylpyridinium dyes tested by Mishra et al. [13].

Generally, we observe a negative solvatochromism in the absorption (blue-shift in absorption with increasing polarity of the solvent), a positive solvatochromism in the emission (red-shift in the emission with increasing polarity of solvent).

The fluorescence quantum yield of eighteen SH dyes is reported in Table 2. The fluorescence quantum yield of tested dyes is in the range from 3×10^{-3} to 0.7. The highest fluorescence quantum yield among the eighteen dyes studied demonstrates SH14 (Table 2).

The electrochemical reduction and oxidation potentials for the SH dyes were determined by cyclic voltammetry using platinum electrode in acetonitrile solution. The one electron oxidation of SH1–SH21 occurs in the range of 0.61–1.06 V. The one electron reduction of these dyes occurs in the range from −1.11 to −0.895 V. The electrochemical oxidation and reduction peaks were quasi-reversible indicating that the oxidized and reduced dye molecules are kinetically unstable [4].

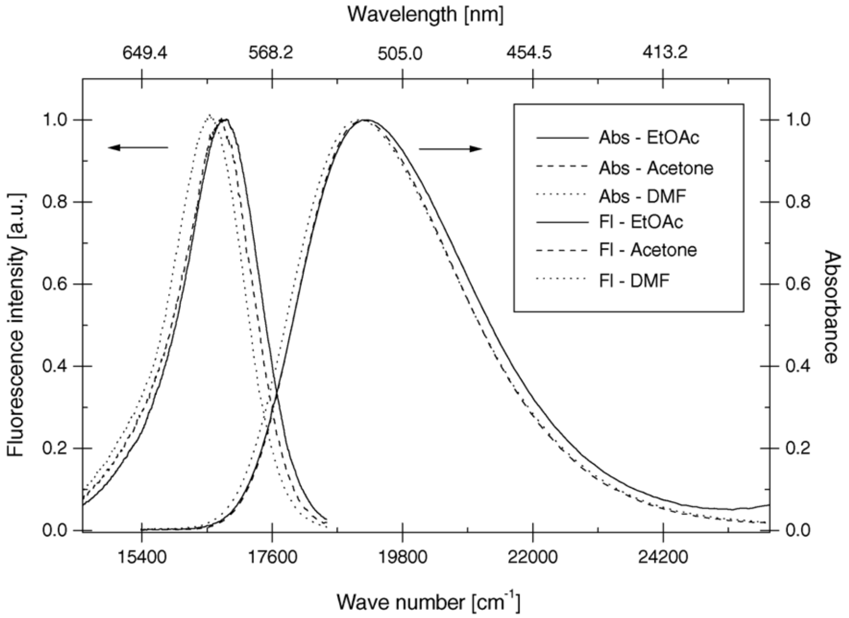


Fig. 1. Absorption and emission spectra of 1×10^{-6} M solution of SH1 in: ethyl acetate (full line), acetone (dashed line) and DMF (dotted line). All the spectra were measured in a 10 mm thick quartz-cuvette.

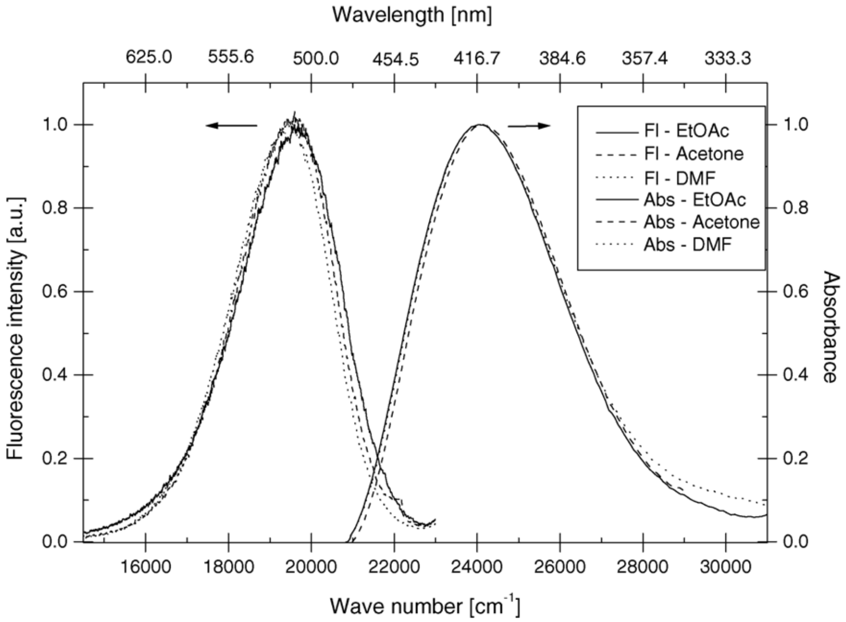


Fig. 2. Absorption and emission spectra of 1×10^{-6} M solution of SH16 in: ethyl acetate (full line), acetone (dashed line) and DMF (dotted line). All the spectra were measured in a 10 mm thick quartz-cuvette.

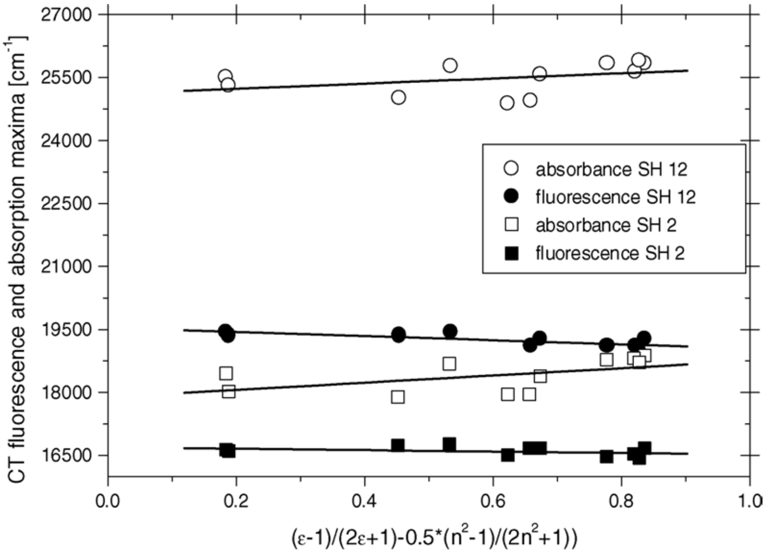


Fig. 3. Solvatochromic shift related to the CT absorption (open signs) and fluorescence maxima (solid signs) for SH2 and SH12, respectively, as a function of solvent polarity.

4. Conclusions

The synthesis and the spectroscopic characterization of newly synthesized hemicyanine dyes, 3-ethyl-(2-*p*-substitued styryl)benzothiazole iodides (SH) are reported. The simple method of synthesis of this class of the dyes opens wide possibility for easy modification of their chemical structures and properties in the desired direction.

The results presented in this paper suggest good prospects for the using of 3-ethyl-2-(*p*-substitued styryl)benzothiazolium iodides as fluorescence probes for various purposes. The absorption, fluorescence emission spectra of studied hemicyanine dyes were investigated in organic non-protic solvents. The intramolecular charge transfer from side aromatic ring to the benzothiazole moiety takes place at excitation of hemicyanine molecules. The electronic and steric effects of substituents have their clear reflection in the electronic spectra of several representatives of the series studied, which is demonstrated by the increase of the Stokes shifts.

Acknowledgment

This work was supported by the State Committee for Scientific Research (KBN) (grant nos. 4 T09A 16024 and BW 20/2002).

References

[1] V.G. Pivovarenko, A.V. Grygorovyvh, V.F. Valuk, A.O. Doroshenko, J. Fluoresc. 6 (2003) 479–487.
[2] A.A. Ischenko, N.A. Derevyanko, V.A. Svidro, Opt. Spectrosc. 72 (1992) 60.
[3] A. Mishra, R.K. Behera, B.K. Mishra, G.B. Behera, J. Photochem. Photobiol. A 116 (1998) 79.
[4] A.S.R. Koti, B. Bhattacharjee, N.S. Haram, R. Das, N. Periasamy, N.D. Sonawane, D.W. Rangnekar, J. Photochem. Photobiol. A. Chem. 137 (2000) 115–123.
[5] L.M. Loew, L.L. Simpson, Biophys. J. 34 (1981) 353.
[6] H. Ephardt, P. Fromherz, J. Phys. Chem. 93 (1989) 7717.
[7] R. Gawinecki, S. Andrzejak, A. Puchała, Org. Prep. Proc. Int. 30 (1998) 455.
[8] F.M. Hamer, J. Chem. Soc. (1956) 1480–1498.
[9] U. Narang, Ch.F. Zhao, J.D. Bhawalkar, F.V. Bright, P.N. Prasad, J. Phys. Chem. 100 (1996) 4521–4525.
[10] S. Chatterjee, P. Gottschalk, P.D. Davis, G.B. Schuster, J. Am. Chem. Soc. 110 (1988) 2326.
[11] J. Olmsted, J. Phys. Chem. 83 (1979) 2581–2584.
[12] K. Binnemans, C. Bex, A. Venard, H. De Leebeeck, C. Görller-Walrand, J. Molec. Liq. 83 (1999) 283–294.
[13] A. Mishra, G.B. Behera, M.M.G. Krishna, N. Periasamy, J. Luminesc. 92 (2001) 175–188.
[14] S. Ozςelik, J. Luminesc. 96 (2002) 141–148.
[15] M. Szczepan, W. Rettig, Y.L. Bricks, Y.L. Słomiński, A.I. Tolmachev, J. Photochem. Photobiol. A 124 (1999) 75–84.
[16] L. Onsager, J. Am. Chem. Soc. 58 (1936) 1486.