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Hemicyanine dyes: synthesis, structure and photophysical properties

Beata Jędrzejewska, Janina Kabatc, Marek Pietrzak, Jerzy Pączkowski*

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

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Abstract

The cationic hemicyanine dyes: 3-ethyl-2-[4-(*N*,*N*-dialkylamino)-styryl]-benzoxazolium salts, 2-[4-(*N*,*N*-dialkylamino)-styryl]-1-(4-iodobenzyl)pyridinium salts and 2-[4-(*N*,*N*-dialkylamino)-styryl]-1-methyl-6-iodopyridinium salts were synthesized and characterized. The dyes were prepared by the condensation of 3-ethyl-2-methylbenzoxazole salts, 1-(4-iodobenzyl)-2-methylpyridinium salts or 1,2-dimethyl-6-iodopyridinium salts with *p*-(*N*,*N*-dialkylamino)-benzaldehydes. Three groups of chromophores with the same acceptor group but with various donor groups were obtained. The spectroscopic properties of the prepared dyes were determined in organic solvents.

Keywords: Hemicyanine dye; Synthesis; Spectroscopic properties; The Stokes shift

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1. Introduction

Hemicyanine dyes (HD) are widely applied in different areas of technology due to their diversified properties. Because of their spectroscopic properties they are commonly used as laser dyes and fluorescence probes. In medicine hemicyanine and related dyes are employed as fluorescence indicators of neurons properties due to their strong charge shift upon light excitation. This property can also be used to detect the variations in the membrane potentials of biological materials. Furthermore, their strong viscosity dependence on the photophysical properties also offers several applications in polymer science and analytical chemistry [1–3].

It is known from literature that certain combinations of organoborate and *N*-alkoxypyridinium salts with cationic unsymmetric cyanine dyes are known to be the effective radical photoinitiators of polymerization in the visible light region [4,5].

In this work the synthesis and properties of three series of hemicyanine dyes are described. The effect of the dyes structure on their spectroscopic properties is discussed as well.

2. Experimental

2.1. Materials

2-Methylbenzoxazole, 2-methylpyridine, 2-bromo-6-methylpyridine, ethyl iodide, methyl iodide, *p*-iodobenzyl bromide and solvents were obtained from Aldrich. Aldehydes, as substrates,

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* Corresponding author.

E-mail address: paczek@atr.bydgoszcz.pl (J. Pączkowski).

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were synthesized according to the procedures given by Gawinecki et al. [6].

2.2. Synthesis

A general route for the synthesis of the prepared hemicyanine dyes is shown in Scheme 1. The condensation of corresponding *p*-(*N*,*N*-dialkylamino)-benzaldehyde with 3-ethyl-2-methylbenzoxazole iodide or ethylsulphate, 1-(4-iodobenzyl)-2-methylpyridinium bromide or 1,2-dimethyl-6-iodopyridinium iodide yielded the following three groups of hemicyanine dyes:

- 3-ethyl-2-[4-(*N*,*N*-dialkylamino)-styryl]-benzoxazolium salts (marked as **A**),
- 2-[4-(*N*,*N*-dialkylamino)-styryl]-1-(4-iodobenzyl)pyridinium bromides (marked as **B**),
- 2-[4-(*N*,*N*-dialkylamino)-styryl]-1-methyl-6-iodopyridinium iodides (marked as **C**).

2.2.1. 3-Ethyl-2-methylbenzoxazole iodide

3-Ethyl-2-methylbenzoxazole iodide was prepared by Hamer's method [7]. The mixture of 2-methylbenzoxazole (1 mol) and ethyl iodide (1.2 mol) was heated at 100 °C for 48 h. After the extraction with dry ether, the crude product was recrystallized from absolute alcohol, washed with ether and dried (yield 75%, mp 195–197 °C).

2.2.2. 1-(4-Iodobenzyl)-2-methylpyridinium bromide

2-Methylpyridine was quaternized with *p*-iodobenzyl bromide by the general method described by Gawinecki et al. [3,8]. The solution of equimolar (0.5 mol) amounts of substrates in 150 ml of acetone was refluxed for 2–3 h. After cooling, the solid product was filtrated off and dried (yield 96%).

2.2.3. 1,2-Dimethyl-6-iodopyridinium iodide

1,2-Dimethyl-6-iodopyridinium iodide was obtained using an analogous method as for 1-(4-iodobenzyl)-2-methylpyridinium bromide starting from 2-iodo-6-methylpyridine and methyl iodide (reflux time 8–10 h, yield 61%).

2.2.4. 3-Ethyl-2-[4-(N,N-dialkylamino)-styryl]-benzoxazolium salts

2.2.4.1. Method 1. To a warm solution of 3-ethyl-2-methylbenzoxazole *p*-toluene-ethylsulphate (0.01 mol) and *p*-*N*,*N*-dialkylaminobenzaldehyde (0.01 mol) in ethanol (6 ml) and a few drops of triethylamine were added. The solution was refluxed for 3 h and then it was treated with potassium iodide or potassium thiocyanate dissolved in warm methanol. The water-washed product was recrystallized from ethanol [9]. This method was applied for the synthesis of compounds: **A1**, **A2** and **A5**.

2.2.4.2. Method 2. A mixture of 3-ethyl-2-methylbenzoxazole iodide (1 mol), *p*-*N*,*N*-dialkylaminobenzaldehyde (1 mol) and acetic anhydride (20 ml) was refluxed for 20 min, then poured into a warm solution of potassium iodide (4 mol) in water (200 ml). The washed with water product was extracted with ether and recrystallized from methanol and ethanol [9]. The earlier described procedure was applied for the synthesis of **A3**, **A6**, **A7**, **A8** and **A9**.

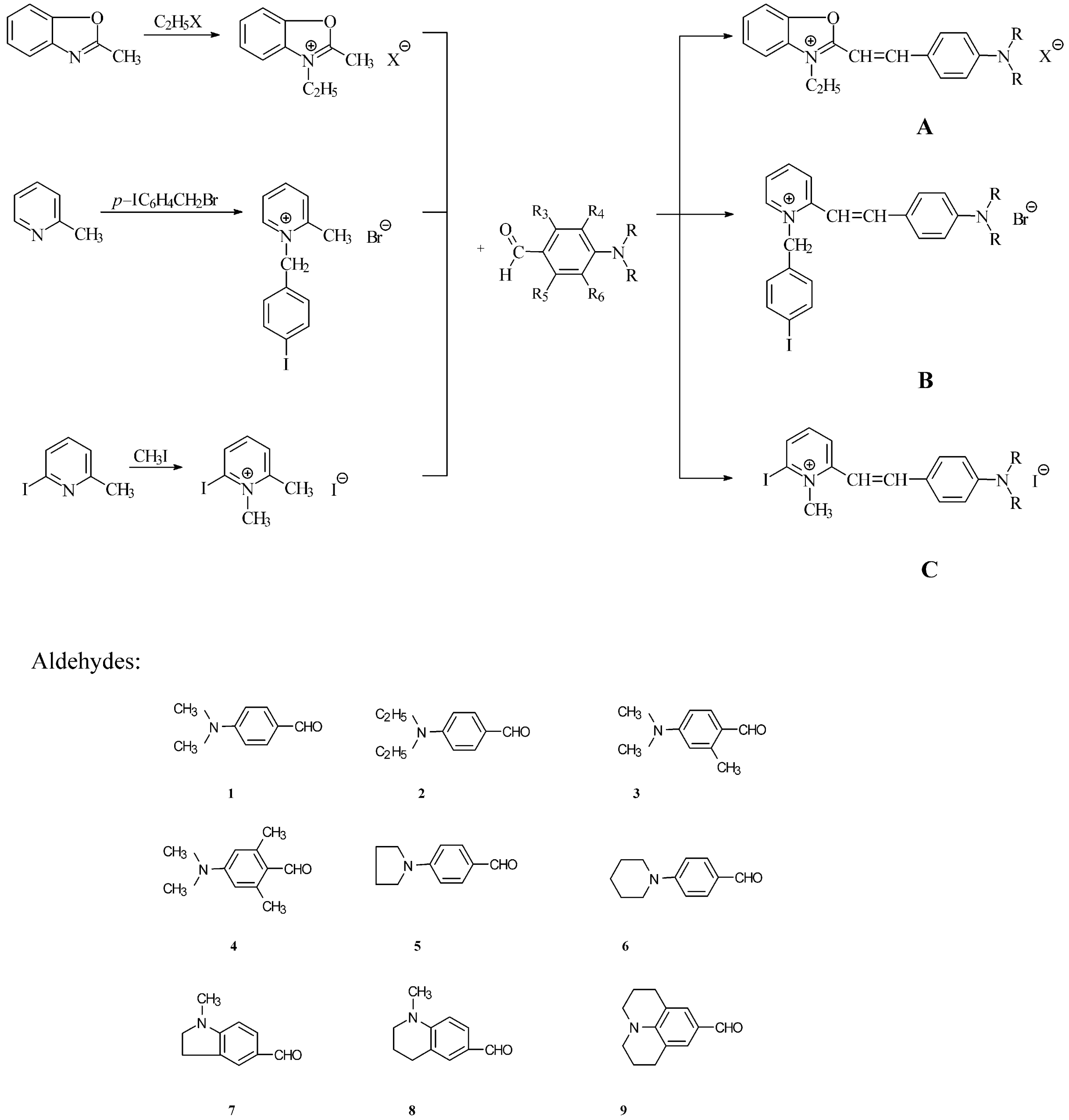
2.2.5. 2-[4-(N,N-dialkylamino)-styryl]-1-(4-iodobenzyl)pyridinium bromides and 2-[4-(N,N-dialkylamino)-styryl]-1-methyl-6-iodopyridinium iodides

Styrylpyridinium bromides or iodides were obtained by refluxing (1–2 h) an appropriate *p*-aminobenzaldehyde (0.01 mol) with *N*-substituted α-picoline halide (0.01 mol) in methanol (20 ml) in the presence of piperidine (a few drops). The precipitate formed after cooling down the reaction mixture was filtrated out and recrystallized from aqueous ethanol or methanol [3,10,11]. The earlier procedure was employed for the synthesis of hemicyanine dyes of groups **B** and **C**.

The chemical structures (see Table 1) of the synthesized compounds were confirmed by ^{1}H NMR and the elementary analysis. The dye characteristics, including the synthetic and analytical data, are collected in Table 2.

2.3. Measurements

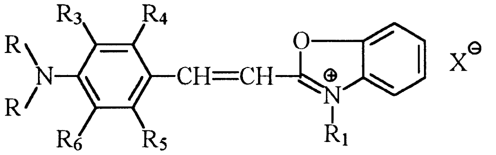
Absorption spectra were recorded with a Varian Cary 3E spectrophotometer, and fluorescence



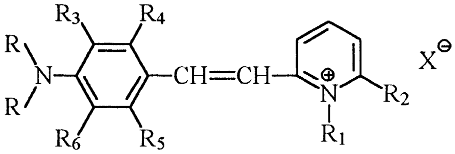
Scheme 1.

spectra were obtained with a Hitachi F-4500 spectrofluorimeter. Absorption and emission spectra were recorded with a spectroscopic quality: acetonitrile, acetone, dimethylformamide (DMF), dichloromethane, tetrahydrofuran (THF), ethyl acetate (EtOAc) and chloroform. The solvents are characterized by their static dielectric constant (ε) at 20 °C and refractive index n_D [12]. The fluorescence measurements were performed at an ambient temperature. The ^1H NMR spectra were recorded with

Table 1
Structures of the hemicyanine dyes synthesized



Group A



Group B, C

Dye	R_2	R_4	R_3	R	R	R_6	R_5	R_1	X	$E_{red}(V)$ SPX[a]
A1		H	H	CH_3	CH_3	H	H	C_2H_5	I	−0.575
A2		H	H	C_2H_5	C_2H_5	H	H	C_2H_5	SCN	−0.550
A3		CH_3	H	CH_3	CH_3	H	H	C_2H_5	I	−0.445
A4		CH_3	H	CH_3	CH_3	H	CH_3	C_2H_5	I	−0.480
A5		H	H	$-(CH_2)_4-$		H	H	C_2H_5	I	−0.470
A6		H	H	$-(CH_2)_5-$		H	H	C_2H_5	I	−0.360
A7		H	$-(CH_2)_2-$		CH_3	H	H	C_2H_5	I	−0.440
A8		H	$-(CH_2)_3-$		CH_3	H	H	C_2H_5	I	−0.460
A9		H	$-(CH_2)_3-$		$-(CH_2)_3-$		H	C_2H_5	I	−0.465
B1	H	H	H	CH_3	CH_3	H	H	p-$IC_6H_4CH_2$-	Br	−0.497
B2	H	H	H	C_2H_5	C_2H_5	H	H	p-$IC_6H_4CH_2$-	Br	−0.565
B3	H	CH_3	H	CH_3	CH_3	H	H	p-$IC_6H_4CH_2$-	Br	−0.507
B4	H	CH_3	H	CH_3	CH_3	H	CH_3	p-$IC_6H_4CH_2$-	Br	−0.540
B5	H	H	H	$-(CH_2)_4-$		H	H	p-$IC_6H_4CH_2$-	Br	−0.445
B6	H	H	H	$-(CH_2)_5-$		H	H	p-$IC_6H_4CH_2$-	Br	−0.520
B7	H	H	$-(CH_2)_2-$		CH_3	H	H	p-$IC_6H_4CH_2$-	Br	−0.550
B8	H	H	$-(CH_2)_3-$		CH_3	H	H	p-$IC_6H_4CH_2$-	Br	−0.545
B9	H	H	$-(CH_2)_3-$		$-(CH_2)_3-$		H	p-$IC_6H_4CH_2$-	Br	−0.530
C1	I	H	H	CH_3	CH_3	H	H	CH_3	I	−0.390
C2	I	H	H	C_2H_5	C_2H_5	H	H	CH_3	I	−0.375
C3	I	CH_3	H	CH_3	CH_3	H	H	CH_3	I	−0.450
C5	I	H	H	$-(CH_2)_4-$		H	H	CH_3	I	−0.450
C6	I	H	H	$-(CH_2)_5-$		H	H	CH_3	I	−0.435
C7	I	H	$-(CH_2)_2-$		CH_3	H	H	CH_3	I	−0.510

[a] Data obtained from cyclic voltametry measurements in an MeCN solution.

the use of a Varian spectrometer Gemini 200 operating at 200 MHz in DMSO solution.

The reduction potentials of hemicyanine dyes were measured by cyclic voltammetry. An Electroanalytical 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

Aromatic aldehydes react with compounds possessing active methyl groups giving the hemicyanine dyes [3,9–11]. For example, the reaction of benzaldehydes with picolines leads to the formation of the corresponding styrylpyridines that can be easily transformed into 1-alkylstyrylpyridinium salts by treatment with alkyl halides [13]. However, this condensation requires a drastic condition, usually a mixture of the reagents with zinc chloride heated at 180–230 °C. What is more the

Table 2
Characteristics of the hemicyanine dyes tested

Dye	Yield (%)	mp (°C)	Empirical formula	NMR δ (DMSO) (ppm)
A1	59	206–210	$C_{19}H_{21}N_2OI$	1.411–1.482 (*t*, 3H, CH_3), 3.094 (*s*, 6H, CH_3), 4.608–4.644 (2H, N–CH_2), 7.284–7.36 (*d*, $J=15.2$ Hz, 1H), 8.288–8.363 (*d*, $J=15$ Hz, 1H), 6.649–6.764 (2H), 7.616–7.663 (2H), 7.966–8.014 (2H), 8.123–8.17 (2H)
A2	46		$C_{22}H_{25}N_3OS$	1.114–1.185 (*t*, 6H, CH_3), 1.416–1.488 (*t*, 3H, CH_3), 3.453–3.557 (4H,–CH_2–), 4.587–4.624 (2H, N–CH_2), 7.295–7.370 (*d*, $J=15$ Hz, 1H), 8.180–8.257 (*d*, $J=15.4$ Hz, 1H), 6.806–6.851 (2H), 7.616–7.664 (2H), 7.868–8.012 (4H)
A3	26	251–253	$C_{20}H_{23}N_2OI$	1.124–1.189 (*t*, 3H, CH_3), 1.415–1.462 (*t*, 3H, CH_3), 3.144 (*s*, 6H, CH_3), 4.638–4.654 (2H, N–CH_2), 7.290–7.42 (*d*, $J=15.2$ Hz, 1H), 8.282–8.357 (*d*, $J=15$ Hz, 1H), 6.642–6.759 (2H), 7.611–7.653 (2H), 7.959–8.010 (2H), 8.113–8.127 (2H)
A4	24	235	$C_{21}H_{25}N_2OI$	1.107–1.175 (*t*, 6H, CH_3), 1.391–1.422 (*t*, 3H, CH_3), 3.125 (*s*, 6H, CH_3), 4.521–4.594 (2H, N–CH_2), 7.184–7.26 (*d*, $J=15.2$ Hz, 1H), 8.228–8.303 (*d*, $J=15$ Hz, 1H), 6.651–6.766 (2H), 7.625–7.669 (2H), 7.991–8.072 (2H), 8.105–8.121 (2H)
A5	67	215–230	$C_{21}H_{23}N_2OI$	1.416–1.488 (*t*, 3H, CH_3), 1.897–1.987 (4H,–CH_2–), 3.362–3.411 (4H,–CH_2–), 4.587–4.623 (2H, N–CH_2), 7.296–7.373 (*d*, $J=15.4$ Hz, 1H), 8.180–8.257 (*d*, $J=15.4$ Hz, 1H), 6.667–6.712 (2H), 7.615–7.661 (2H), 7.889–7.978 (4H)
A6	26	252	$C_{22}H_{25}N_2OI$	1.412–1.482 (*t*, 3H, CH_3), 1.869–1.921 (2H,–CH_2–), 2.722–2.780 (2H,–CH_2–), 3.043 (*s*, 3H, CH_3N–), 4.578–4.614 (2H, N–CH_2–), 7.232–7.308 (*d*, $J=15.2$ Hz, 1H), 8.110–8.186 (*d*, $J=15.2$ Hz, 1H), 6.670–6.716 (1H), 7.606–7.724 (4H), 7.905–7.999 (2H)
A7	53	227	$C_{20}H_{21}N_2OI$	1.402–1.427 (*t*, 3H, CH_3), 2.944 (*s*, 3H, CH_3N), 3.013–3.095 (2H), 3.389–3.442 (2H), 3.651–3.693 (2H), 4.557–4.594 (2H, N–CH_2), 7.205–7.280 (*d*, $J=15$ Hz, 1H), 8.118–8.194 (*d*, $J=15.2$ Hz, 1H), 6.549–6.592 (1H), 7.596–7.728 (3H), 7.806 (1H), 7.896–7.984 (2H)
A8	21	249	$C_{21}H_{23}N_2OI$	1.157–1.490 (*t*, 3H, CH_3), 2.944 (*s*, 3H, CH_3N), 3.389–3.693 (4H, CH_2), 4.557–4.597 (2H, N–CH_2), 6.549–6.592 (1H), 7.102–7.177 (*d*, $J=15$ Hz, 1H), 8.018–8.094 (*d*, 15.2 Hz, 1H), 7.596–7.994 (6H)
A9	23	256	$C_{23}H_{23}N_2OI$	1.074–1.509 (*t*, 3H, CH_3), 3.096–3.150 (4H CH_2N), 3.251–.3713 (6H, CH_2N), 4.456–4.894 (2H, N–CH_2–), 7.208–7.284 (*d*, $J=15.2$ Hz, 1H), 8.131–8.207 (*d*, $J=15.2$ Hz, 1H), 6.670–6.731 (4H), 7.984–8.005 (2H)
B1	66	249–258	$C_{22}H_{22}N_2IBr$	3.024 (*s*, 6H, CH_3N), 6.009 (*s*, 2H,–CH_2–N^+), 7.179–7.258 (*d*, $J=15.8$ Hz, 1H), 7.834–7.911 (*d*, $J=15.4$ Hz, 1H), 6.742–6.785 (*d*, 2H), 7.106–7.147 (*d*, 2H), 7.578–7.622 (*d*, 2H), 7.736–7.777 (3H), 8.406–8.516 (2H), 8.949–8.979 (1H)
B2	77	254–260	$C_{24}H_{26}N_2IBr$	1.084–1.153 (*t*, 6H, CH_3), 3.446–3.482 (4H, CH_2N), 5.974 (*s*, 2H,–CH_2–N^+), 7.823–7.901 (*d*, $J=15.6$ Hz, 1H), 6.710–6.755 (2H), 7.096–7.192 (4H), 7.540–7.585 (2H), 7.744–7.803 (2H), 8.381–8.500 (2H), 8.906–8.935 (1H)
B3	38	263–265	$C_{23}H_{24}N_2IBr$	2.898 (*s*, 6H, CH_3N), 2.068 (*s*, 3H, CH_3), 5.983 (*s*, 2H,–CH_2–N^+), 7.176–7.255 (*d*, $J=15.8$ Hz, 1H), 7.896–7.974 (*d*, $J=15.6$ Hz, 1H), 6.568–6.660 (2H), 7.082–7.123 (2H), 7.680–7.835 (4H), 8.405–8.567 (2H), 8.918–8.945 (1H)

(*continued on next page*)

Table 2 (*continued*)

Dye	Yield (%)	mp (°C)	Empirical formula	NMR δ (DMSO) (ppm)
B4	72	175–178	$C_{24}H_{26}N_2IBr$	2.427 (*s*, 6H, CH$_3$N), 2.068–2.129 (6H, CH$_3$), 6.007 (*s*, 2H,–CH$_2$–N$^+$), 7.163–7.243 (*d*, *J* = 16 Hz, 1H), 7.786–7.867 (*d*, *J* = 16.2 Hz, 1H), 6.850–7.163 (3H), 7.668–7.772 (3H), 8.051–8.103 (1H), 8.627–8.645 (2H), 9.110–9.175 (1H)
B5	84	266–271	$C_{23}H_{20}N_2IBr$	1.942–2.006 (4H,–CH$_2$–), 3.279–3.338 (4H,–CH$_2$–N), 5.976 (*s*, 2H,–CH$_2$–N$^+$), 7.205–7.283 (*d*, *J* = 15.6 Hz, 1H), 7.829–7.907 (*d*, *J* = 15.6 Hz, 1H), 6.593–6.637 (*d*, 2H), 7.099–7.141 (*d*, 2H), 7.564–7.608 (*d*, 2H), 7.740–7.781 (3H), 8.385–8.460 (2H), 8.904–8.934 (1H)
B6	75	261–265	$C_{25}H_{26}N_2IBr$	1.586 (6H,–CH$_2$–), 3.074–3.126 (4H,–CH$_2$–N), 6.011 (*s*, 2H,–CH$_2$–N$^+$), 7.222–7.300 (*d*, *J* = 15.6 Hz, 1H), 7.807–7.887 (*d*, *J* = 16 Hz, 1H), 6.952–6.997 (*d*, 2H), 7.099–7.141 (*d*, 2H), 7.568–7.611 (*d*, 2H), 7.736–7.778 (3H), 8.428–8.479 (2H), 8.955–8.987 (1H)
B7	76	255–258	$C_{23}H_{22}N_2IBr$	2.833 (*s*, 3H, CH$_3$N), 2.939–3.021 (2H,–CH$_2$–), 3.449–3.532 (2H,–CH$_2$–N), 5.986 (*s*, 2H,–CH$_2$–N$^+$), 7.136–7.213 (*d*, *J* = 15.4 Hz, 1H), 7.809–7.887 (*d*, *J* = 15.6 Hz, 1H), 6.487–6.528 (*d*, 1H), 7.382–7.388 (2H), 7.429–7.503 (2H), 7.737–7.793 (3H), 8.374–8.451 (2H), 8.904–8.934 (1H)
B8	60	262–267	$C_{24}H_{24}N_2IBr$	2.901 (*s*, 3H, CH$_3$N), 1.859–2.067 (2H,–CH$_2$–), 2.709–2.772 (2H,–CH$_2$–), 3.360–3.454 (2H,–CH$_2$–N), 5.954 (*s*, 2H,–CH$_2$–N$^+$), 7.233–7.311 (*d*, *J* = 15.6 Hz, 1H), 7.925–7.847 (*d*, *J* = 15.6 Hz, 1H), 6.593–6.638 (*d*, 2H), 7.095–7.137 (2H), 7.381–7.430 (2H), 7.745–7.786 (2H), 8.370–8.435 (2H), 8.867–8.900 (1H)
B9	65	234–242	$C_{26}H_{26}N_2Ibr$	1.848–1.862 (4H,–CH$_2$–), 2.655–2.712 (4H,–CH$_2$–), 3.237–3.290 (4H,–CH$_2$–N), 5.953 (*s*, 2H,–CH$_2$–N$^+$), 7.034–7.103 (1H), 7.743–7.785 (1H), 7.144 (4H), 7.713 (3H), 8.326–8.401 (2H), 8.853–8.885 (1H)
C1	70	148–152	$C_{16}H_{18}N_2I_2$	3.011 (*s*, 6H, CH$_3$N), 4.009 (*s*, 3H, CH$_3$N$^+$), 7.069–7.148 (*d*, *J* = 15.8 Hz, 1H), 6.758–6.803 (*d*, 2H), 7.298–7.339 (*d*, 1H), 7.608–7.650 (*d*, 3H), 7.826–7.866 (*d*, 1H), 8.142 (1H)
C2	33	166–168	$C_{18}H_{22}N_2I_2$	1.081–1.152 (*t*, 6H, CH$_3$), 3.138–3.210 (4H,–CH$_2$N), 4.001 (*s*, 3H, CH$_3$N$^+$), 7.020–7.100 (*d*, *J* = 16 Hz, 1H), 7.637–7.717 (*d*, *J* = 16 Hz, 1H), 6.718–6.763 (*d*, 2H), 7.277–7.319 (*d*, 1H), 7.760–7.621 (2H), 7.820–7.862 (1H), 8.090–8.130 (1H)
C3	18	188–191	$C_{17}H_{20}N_2I_2$	2.993 (*s*, 6H, CH$_3$N), 4.009 (*s*, 3H, CH$_3$N$^+$), 2.436 (*s*, 3H, CH$_3$), 7.015–7.094 (*d*, *J* = 15.8 Hz, 1H), 7.812–7.890 (*d*, *J* = 15.8 Hz, 1H), 6.594–6.725 (*d*, 2H), 7.221–7.349 (*d*, 1H), 7.730–7.812 (2H), 8.004–8.143 (1H)
C5	34	187–190	$C_{18}H_{22}N_2I_2$	4.009 (*s*, 3H, CH$_3$N$^+$), 1.974–2.007 (4H,–CH$_2$–), 3.212– 3.318 (4H,–CH$_2$–N), 7.040–7.119 (*d*, *J* = 15.8 Hz, 1H), 7.661–7.737 (*d*, *J* = 15.8 Hz, 1H), 6.600–6.644 (*d*, 2H), 7.279–7.316 (*d*, 1H), 7.604–7.647 (2H), 7.833–7.868 (*d*, 1H), 8.094–8.130 (1H)
C6	31	150–154	$C_{19}H_{22}N_2I_2$	4.010 (*s*, 3H, CH$_3$N$^+$), 1.586 (6H,–CH$_2$–), 2.983–3.228 (4H,–CH$_2$–N), 7.107–7.185 (*d*, *J* = 15.6 Hz, 1H), 7.632–7.708 (*d*, *J* = 15.2 Hz, 1H), 6.971–7.016 (*d*, 2H), 7.327–\7.368 (*d*, 1H), 7.600–7.631 (2H), 7.823–7.863 (*d*, 1H), 8.117–8.157 (1H)
C7	25	160–165	$C_{17}H_{18}N_2I_2$	4.000 (*s*, 3H, CH$_3$N$^+$), 2.815 (*s*, 3H, CH$_3$N), 2.934–3.013 (2H,–CH$_2$–), 3.411–3.493 (2H,–CH$_2$–N), 7.036–7.115 (*d*, *J* = 15.8 Hz, 1H), 7.634–7.712 (*d*, *J* = 15.6 Hz, 1H), 6.507–6.548 (*d*, 1H), 7.279–7.322 (*d*, 1H), 7.390–7.433 (2H), 7.815–7.856 (*d*, 1H), 8.091–8.130 (1H)

efficiency of the stilbazole derivatives formation is low. Alternatively, the use of quaternary salts instead of picoline in a small amount of alcohol and in the presence of few drops of piperidine gives the condensation product in a crystalline form with a high yield [10,11]. This type of approach was first time described by König in 1912 [14].

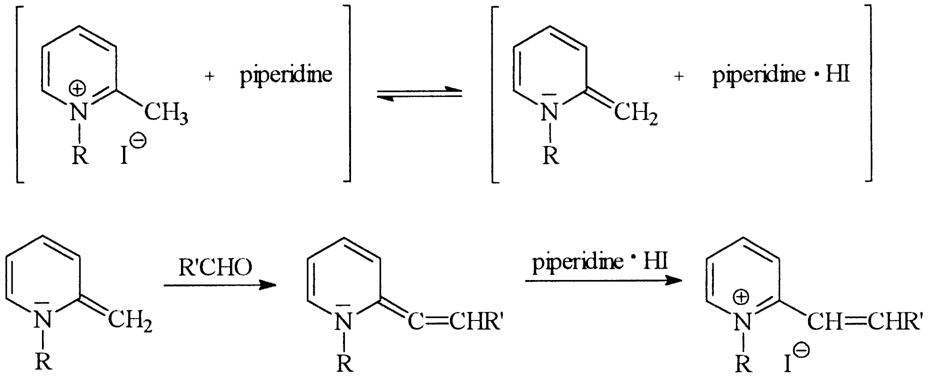
In this paper, dyes were obtained by the method given by Phillips [10,11] and Hamer [7,9] (Knoevenagel condensation) according to the reactions presented in Scheme 1.

Mills and Raper [15] suggested the following mechanism of the reaction (see Scheme 2). According to this scheme, in the first step, hydrogen iodide is removed from quaternary salt by a stronger base (piperidine), yielding piperidine hydrogen iodine and methenyldihydropyridine. This intermediate is more reactive and it reacts with benzaldehyde giving allene which withdraws hydrogen iodide from piperidine. As the final product the 1-alkyl-2-styrylpyridinium salt is obtained. On the basis of this reaction, three series of new stilbene-type derivatives with various electron donor groups (*N*,*N*-dialkylamino group) and the same acceptor residue (benzoxazole or pyridine rings) have been synthesized (see Scheme 1 and Table 1) and characterized.

The condensation of *N*-alkyl substituted 2-methylbenzoxazol or 1,2-dimethylpyridine with seven different aminobenzaldehydes was used for the preparation of all the dyes. The synthesis were carried out in the presence of triethylamine (dyes **A1**, **A2**, **A5**) or piperidine (compounds of **B** and **C** groups), respectively. The yield of the reaction oscillated in the range 20–84% and often depended on the type of an anion of cycloammonium salts. In almost all the cases the exchange of iodide or bromide anion on *p*-toluene-ethylsulphate increases the yield of the reaction from about 2 to 50% [16]. The addition of potassium iodide to the solution gave less soluble salts in organic solvents. To our best knowledge, the majority of the synthesized compounds have not been described in literature, yet.

The structure and purity of the prepared compounds were confirmed by NMR spectroscopy and thin layer chromatography. The structural analysis of the dyes is presented in Table 2. The inspection of the data from Table 2 shows that the melting points for numerous compounds are not sharp. This can be attributed to the liquid crystal properties of the hemicyanine dyes [17]. It is noteworthy that the ^{1}H NMR spectra (Table 2) 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 ($J\approx15$ Hz), indicates the *trans* form of the ground state of the synthesized dyes. The data characterizing the spectra of all the prepared compounds presented in Table 1 also shows all the relevant protons (see Table 2).

Figs. 1–6 show the illustrative electronic absorption and the fluorescence emission spectra for the selected hemicyanine dyes in ethyl acetate solution. Table 3 collects the values of the



Scheme 2.

absorption maximum positions, molar absorption coefficients and Stokes shifts for the tested dyes. The electronic absorption spectra of all the three groups of compounds display a broad band with maximum in the range from 400 to 500 nm and molar absorption coefficient of about 17 000 (dm^3 mol^{-1} cm^{-1}) for series **A** and about 30 000 (dm^3 mol^{-1} cm^{-1}) for series **B** and **C**, respectively. The inspection of the absorption spectra presented in Figs. 1 and 2 show that the position of the π–π* absorption band strongly depends on the molecular structure of the dye.

Fig. 1 presents the normalized absorption spectra in ethyl acetate of the three selected dyes from group **A**. The spectra of the dyes (**A2**, **A5**, **A7**) are very similar in shape and position in the solvent applied (see Fig. 1). In ethyl acetate the maximum absorption position and Stokes shift (Table 3) usually show a value less than 10 nm and this indicates that the electronic transition of the

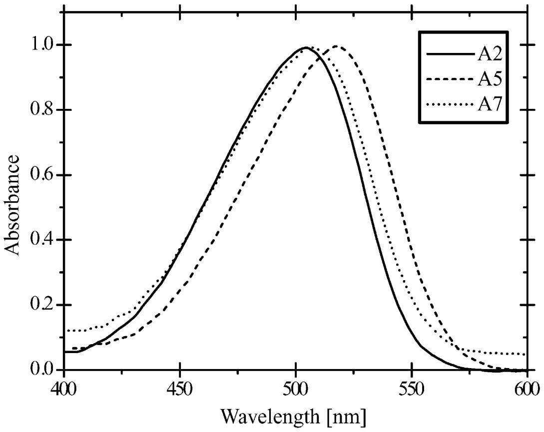


Fig. 1. Electronic absorption spectra of selected dyes in ethyl acetate at 293 K. The chromophores are end-capped with the same acceptor group and with different donor groups (marked in the figure).

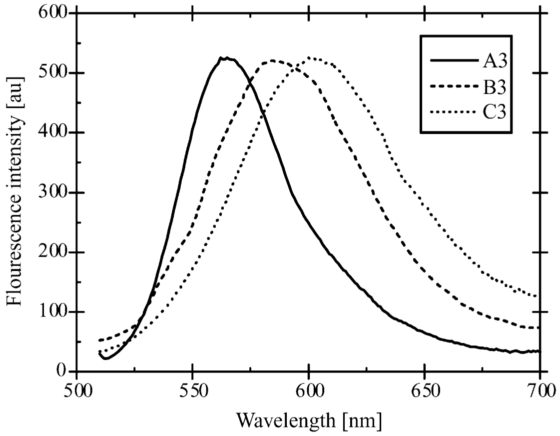


Fig. 3. Fluorescence spectra of selected dyes in ethyl acetate at 293 K. The chromophores are end-capped with the same acceptor group and with different donor groups (marked in the figure).

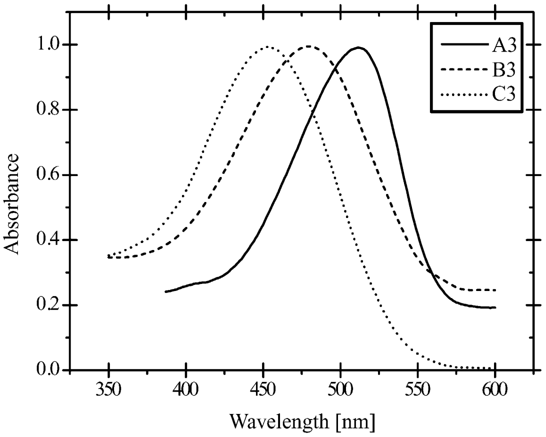


Fig. 2. Electronic absorption spectra of selected dyes (marked in the figure) in ethyl acetate at 293 K. The applied dyes possess the same donor group and various acceptor groups.

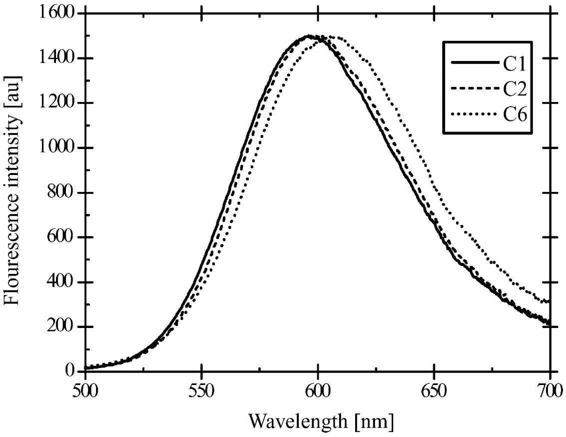


Fig. 4. Fluorescence spectra of selected dyes (marked in the figure) in ethyl acetate at 293 K. The applied dyes possess the same donor group and various acceptor groups.

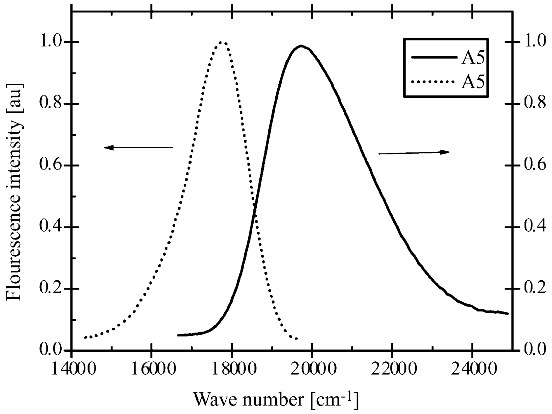


Fig. 5. Electronic absorption and fluorescence emission spectra of the dye (**A5**). Spectra recorded in ethyl acetate at 293 K.

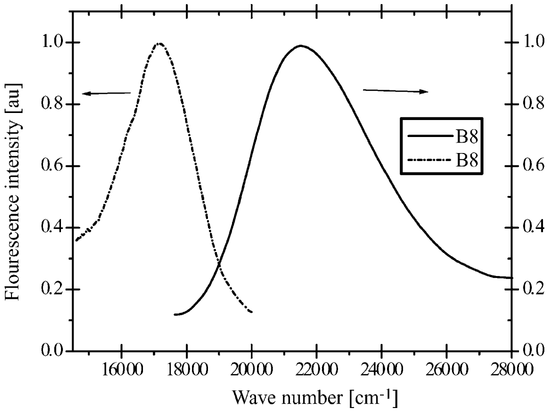


Fig. 6. Electronic absorption and fluorescence emission spectra of the dye (**B8**). Spectra recorded in ethyl acetate at 293 K.

Table 3
Spectroscopic properties of the hemicyanine dyes tested in ethyl acetate as a solvent

Dye	$\lambda^{A}_{\max}$ (nm)	ε (dm^3 mol^{-1} cm^{-1})	$\lambda^{Fl}_{\max}$ (nm)	Stokes shift (cm^{-1})
A1	498	15 500	559.2	2200
A2	506	21 000	560.0	1970
A3	512	14 500	561.6	1700
A4	504	17 000	565	2200
A5	508	17 500	563.6	1900
A6	507	12 000	567.2	2100
A7	519	17 000	570.8	1800
A8	522	13 000	575.2	1800
A9	503	17 000	567	2300
B1	472	38 000	597.0	4400
B2	483	38 000	587.8	3690
B3	478	24 500	595.2	4100
B4	–	13 000	–	–
B5	483	38 000	603.6	4100
B6	458	34 000	602.2	5200
B7	481	33 000	611.8	4400
B8	493	35 000	608.6	3900
B9	507	35 500	618.4	3600
C1	448	28 500	596.0	5500
C2	462	28 000	600.4	4990
C3	456	22 000	600.2	5300
C5	458	38 000	601.4	5200
C6	436	24 500	605.2	6400
C7	463	25 500	601.6	4700

The molar coefficient for groups **B** and **C** is obtained in DMF.

hemicyanine chromophores is not significantly perturbed by the electron donor moiety. But the exchange of benzoxazolium moiety on pyridinium one causes a significant variation in the maximum position (512, 478, 456 nm for **A3**, **B3** and **C3**, respectively; see Fig. 2) and it dramatically increases the Stokes shift (see Table 3). It is worth noting that the localization of a heavy atom at the pyridinium moiety affects the absorption maximum position (see Table 3). The absorption spectrum of the hemicyanines possessing a heavy atom at the pyridinium ring is more shifted to the blue in comparison to the dyes from group **B**. In this case the heavy atom effect should be treated more likely as an external effect because of its side alkyl chain placement.

Similarly, as for the group of the styrylpyridinium dyes tested by Gawinecki et al. [3,6], the substitution in *orto* position to the –CH=CH– group (compounds **B3**, **B4** and **C3**) forms a pretwisted molecule even in the ground state. This is reflected in the electronic absorption spectra where a blue shift is observed in comparison to the model dye. This effect is caused by a steric interaction, which decouples the dimethylamino group from the electron-accepting part of the molecule [8]. This feature is not observed for the group of the hemicyanine dyes possessing the benzoxazole ring (group **A**).

Generalizing, the spectra of pyridine derivatives are more broadened with respect to those of benzoxazole derivatives. The selected comparative results are shown in Table 4.

From Table 3 it can also be seen that the maximum of the fluorescence spectra for all chromophores, is located at ~560 nm for series **A** and ~600 nm for series **B** and **C** (an excitation wavelength 470 nm). The illustrative fluorescence emission spectra, presented in Fig. 3, suggest that the electron structure of the donor groups in the molecule does not have a significant effect on the position of the emission band. Fig. 4 depicts the normalized emission spectra for the selected dyes in ethyl acetate. It is apparent from the inspection of these spectra that the structure of the electron accepting group only slightly changes the fluorescence maximum position (562, 595 and 600 nm for dyes **A3**, **B3** and **C3**, respectively, see Table 3). It is also observed that the fluorescence emission spectra of the hemicyanine dyes from group **A** are blue shifted in comparison to the dyes from groups **B** and **C**, although, the absorption spectrum of these dyes are red shifted in comparison to the spectrum of the dyes possessing the pyridinium moiety.

In general, the fluorescence emission spectra bands are somewhat narrower than the absorption spectra (see Table 4). If the broadening of the spectra is understood as deriving from the population of the thermally available conformers, then according to W. Rettig [2], the observed results can be taken as the evidence that some of these conformers are nonemissive (reduction of fluorescence width). The twisting of the olefinic double bands gives this type of a conformer. The deactivation of this state should occur mainly by radiationless processes because the energy gap between its excited state and the ground state is very small [8].

Table 4
The half-width of absorption and emission spectra for selected dyes in ethyl acetate

Dye	Half-width of absorption band (cm^{-1})	Half-width of fluorescence band (cm^{-1})
A2	1222	760
A3	1170	721
A7	1230	734
B2	1758	1012
B3	1779	1067
B7	1782	1041
C2	2003	1009
C3	2118	1064
C7	2293	1152

The difference in energy between the absorbed and emitted radiation is known as the Stokes shift [18]. Figs. 5 and 6 present the UV–visible absorption and emission spectra of **A5** and **B8** dyes in ethyl acetate. The emission spectrum exhibits a mirror image of the absorption spectrum with a small Stokes shift for **A5** (1900 cm^{-1}) and a large Stokes shift for **B8** (3900 cm^{-1}). Generally, a large Stokes shift is attributed to a different charge distribution (or geometry) in the excited state compared to the ground state [18,19]. On the basis of quantum chemical calculations, Fromherz [20] reported, for the hemicyanine dyes that the positive charge of the chromophore is displaced upon the excitation from the pyridinium moiety towards the amino moiety. This is not observed in the dyes of group **A**. It means that the geometry of the ground state for these dyes is similar to the geometry of the excited state.

An important question to be addressed in interpreting the fluorescence spectroscopic results in organic solvent is the identification of the structure for the dye in different solvents. The zwitterionic hemicyanine dyes consist of a positively charged chromophore and a negative counterion as shown in Scheme 1. Hemicyanine dyes exhibit a significant charge displacement when the molecules are excited from the ground state to the excited state. This large charge displacement is an indication of a large polarizability [21]. Therefore, the absorption and emission spectra of the hemicyanine dyes depends on the polarity of the solvent. This solvatochromism is assigned generally to the change of the molecular dipole moment upon the electronic excitation and the interaction of the dipole moment with the polarizable environment [22].

Fluorescencing molecules such as the ones studied in this work possess the possibility of multiple structures because of the flexibility of the styryl bond and this should be reflected in their Stokes shift. The results of the spectroscopic measurements performed for studied dyes in organic solvents are

Table 5
Spectroscopic properties of the hemicyanine dyes tested in different solvents

Solvent	A2			B2			C2		
	λ_{ab} (nm)	λ_{fl} (nm)	Stokes Shift (cm^{-1})	λ_{ab} (nm)	λ_{fl} (nm)	Stokes Shift (cm^{-1})	λ_{ab} (nm)	λ_{fl} (nm)	Stokes Shift (cm^{-1})
Acetonitryle	502	562.4	2140	484	615.2	4400	461	597.4	4960
Acetone	502	562	2130	486	611	4210	462	603	5060
DMF	503	569	2310	485	612.2	4280	465	601.4	4880
Dichloromethane	528	564.8	1230	524	602	2470	492	586.8	3280
THF	509	563.8	1910	484	598	3940	468	599.6	4690
Ethyl acetate	506	560	1970	483	587.8	3690	462	600.4	4990
Chloroform	525	567.8	1440	505	571.6	2530	486	598.6	3870

presented in Table 5. There are three possible structures of hemicyanine dye (*trans, quinoid* and *cis*). Even though the *trans* and *quinoid* structures are mesomeric resonance structures, it should be noted that for two isomers the positive charge is localized on different types of nitrogen: on the benzoxazole or pyridine nitrogen in *trans* isomer and on the amine nitrogen in the *quinoid* form. As a result, solvents of different polarity may interact differently with the two isomers, making it possible that either *trans* or *quinoid* forms are present in various solvents. Therefore, one has to examine the experimental spectroscopic data in a variety of organic solvents to identify multiple structures for the dye in the ground state.

The absorption and emission spectra of the tested dyes are perturbed by the organic solvents. The spectral maximum positions for the absorption and emission spectra are given in Table 5 for three representative dyes, namely **A2**, **B2** and **C2**, respectively. Stokes shift is one of the quantitative parameters which is useful to understand the origin of the variation of spectral shift in organic solvents. The Stokes shift values are also given in Table 5. The highest value of Stokes shift (>4000 cm^{-1}) was observed in acetonitrile, acetone and DMF for the dyes from group **B** and in acetonitile, acetone, DMF, THF, ethyl acetate for the dyes from group **C**. The lowest values of Stokes shift was observed in dichloromethane and chloroform for all the tested dyes. The hemicyanine dyes possessing a benzoxazole ring show a lower value of Stokes shift in comparison to the hemicyanine dyes possessing a pyridine ring (1200÷2300 cm^{-1}).

A plot of Stokes shift versus the polarity parameter, Δf (Lippert–Mataga relationship [23], Fig. 7) shows the presence of the correlation between Stokes shift and Δf for all the tested dyes. A linear dependence of Stokes shift and Δf for all the solvents confirms that the dyes have one structure in the ground and one in the excited states and that the slope of these relationships depends on the change of the dipole moment upon the excitation [24].

The absorption spectrum of zwitterionic hemicyanine dyes is shifted to the blue and their fluorescence spectrum is shifted to the red by solvents of high polarity (Table 5, Figs. 8 and 9). It should stress that only in the case of the hemicyanine dyes from group **B** the fluorescence spectrum is shifted to the blue by solvents of high polarity (Fig. 9).

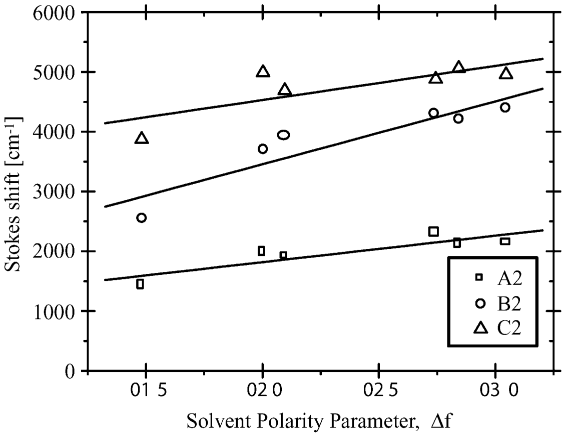


Fig. 7. The relationship between Stokes shift and the solvent polarity parameter, Δf for selected dyes.

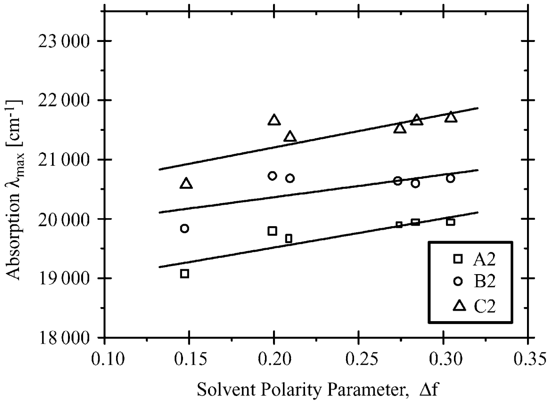


Fig. 8. The Lippert–Mataga relationship for selected dyes (marked in the figure).

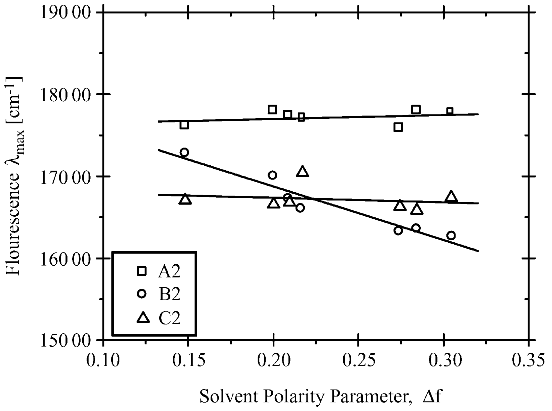


Fig. 9. The Lippert–Mataga relationship for marked in the figure dyes.

In summary of the analysis of spectroscopic properties, it should be noted that: (1) the tested dyes upon the excitation increase their dipole moment, (2) the tested dyes are polar in their ground state, for example, they have a permanent ground state dipole moment.

Acknowledgements

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