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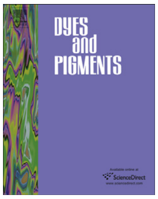

The synthesis and spectroscopic studies of new aniline-based squarylium dyes

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ABSTRACT

The synthesis and spectroscopic properties of series of new aniline–based squarine dyes have been presented. The effect of solvent polarity, hydrogen bonding and substituent on spectroscopic properties of 1,3-*bis*(phenylamino)squarine (**SQG1**), 1,3-*bis*(4-bromophenylamino)squarine (**SQG2**), 1,3-*bis*(4-ethylphenylamino)squarine (**SQG3**), 1,3-*bis*(4-ethoxyphenylamino)squarine (**SQG4**), 1,3-*bis*(4-nitrophenylamino)squarine (**SQG5**), 1,3-*bis*(4-chlorophenylamino)squarine (**SQG6**), 1,3-*bis*(4-iodophenylamino)squarine (**SQG7**), 1,3-*bis*(4-aminobenzosulfo)squarine (**SQG8**) 1,3-*bis*(4-methylphenylamino)squarine (**SQG9**) 1,3-*bis*(4-hydroxyphenylamino)squarine (**SQK1**) in ten selected solvents were studied.

1. Introduction

Development of new dyes, which have a panchromatic or abroad absorption bands in visible region, make a possibility of application them in wide modern technologies such as radiation curing [1–10], imaging and optics technologies, medicine [11,12], electronics, nanotechnology and new advances materials produce, photovoltaics, photodynamic therapy and pharmaceutical industry [13–19]. The squarylium dyes possess a D-A-D structure classified to polymethine dyes including the butenedione core linked with two the same substituent in symmetrical squarine [20] and with two different groups in asymmetrical squarine [21].

The squarylium dyes demonstrated three resonance structures with all-aromatic zwitterion and two tautomeric cyanine type structures [22].

In present paper, the series of *p*-aniline based squarine dyes are synthesized and their spectroscopic properties in different solvents are described. The effect of both solvents and substituents on the absorption properties of *p*-substituted aniline based squarine dyes has been determined.

2. Materials and methods

2.1. Synthesis

The substrates used for synthesis of squarine dyes were purchased from Sigma-Aldrich (Poland) and were used without further purification. The squarylium dyes: 1,3-*bis*(phenylamino)squarine (**SQG1**), 1,3-*bis*(4-bromophenylamino)squarine (**SQG2**), 1,3-*bis*(4-ethylphenylamino)squarine (**SQG3**), 1,3-*bis*(4-ethoxyphenylamino)squarine (**SQG4**), 1,3-*bis*(4-nitrophenylamino)squarine (**SQG5**), 1,3-*bis*(4-chlorophenylamino)squarine (**SQG6**), 1,3-*bis*(4-iodophenylamino)squarine (**SQG7**), 1,3-*bis*(4-aminobenzosulfo)squarine (**SQG8**), 1,3-*bis*(4-methylphenylamino)squarine (**SQG9**); 1,3-*bis*(4-hydroxyphenylamino)squarine (SQK1) were synthesized according to literature procedure described in work [20]. The general route of synthesis is shown in Scheme 1.

2.1.1. General procedure for synthesis of SQG1, SQG2, SQG3, SQG4, SQG6, SQG7, SQG9, SQK1

The synthesis of squarine dyes is based on the condensation reaction of squaric acid with *p*-substituted aniline derivatives. 1,2-Dihydroxycyclobuten-3,4-dione (2.5 mmol, 0.29 g) was heated under reflux in a mixture of 1-butanol (40 mL) and toluene (20 mL), and water was distilled off azeotropically using a Dean-Stark trap. After 1 h, the appropriate *p*-aniline (5 mmol) was added and the reaction mixture refluxed for additional 4 h [20]. Reaction mixture

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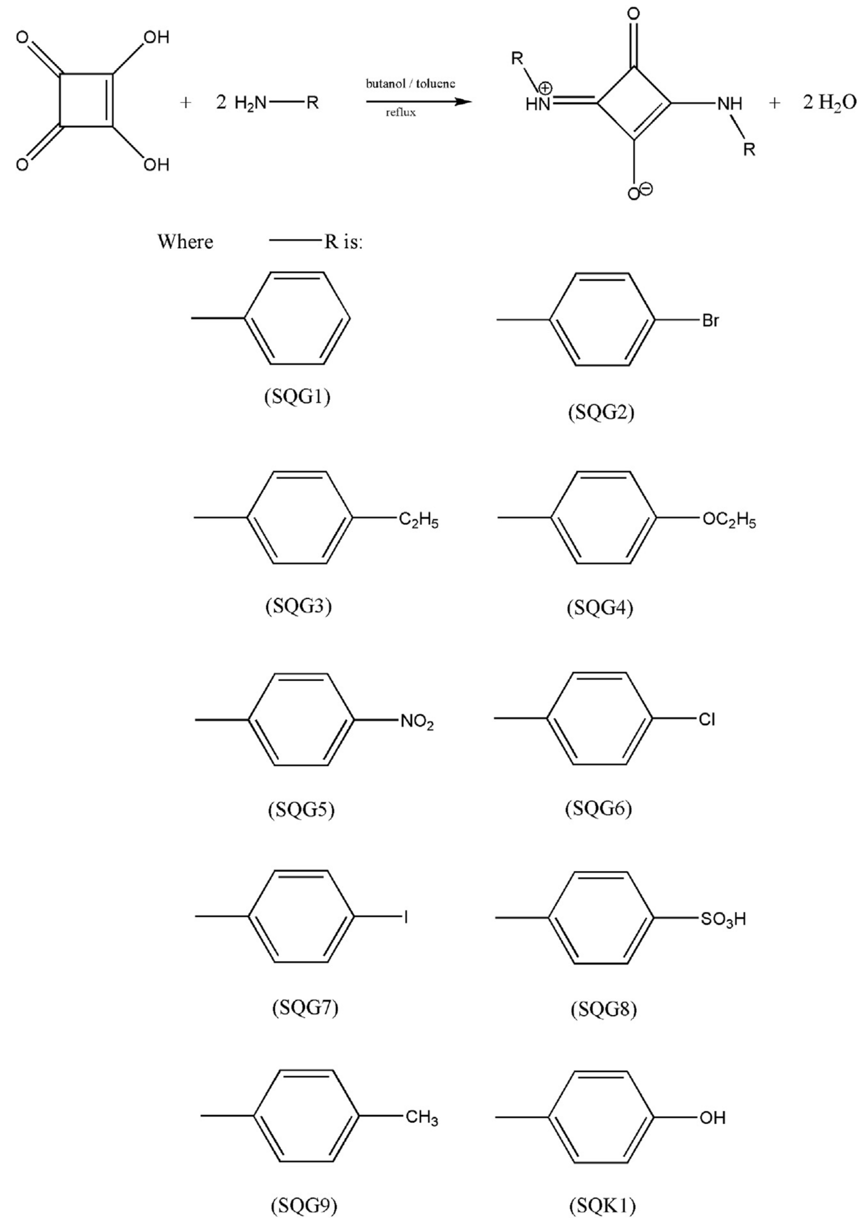

Scheme 1. Synthesis of squarine dyes.

was cooled and the solvent removed on a Büchner funnel. The solid dried in room temperature.

1,3-*Bis*(phenylamino)squarine (**SQG1**) was prepared with general procedure from aniline (5 mmol; 0.45 mL) gave as solid yellow (0.38 g, 58.15%.), mp. 328 °C. ^{1}H NMR (DMSO−d_6), δ (ppm): 7.1196−7.1566 (t, 2H, Ar); 7.3625−7.4021 (t, 4H, Ar); 7.7874−7.8073 (d, $J \approx$ 7.96 Hz, 4H, Ar); 11.2766 (s, 2H, -NH-). IR (KBr; cm^{-1}): 3087.87, 3058.58, 2992.99, 2967.42 (=C-H); 2777.99, 2746.84, 2680.45 (NH$_2^+$); 1615.30, 1591.09 (C=O); 1552.29 (N-H); 1499.64, 1450.55, 1425.97, 1410.77 (C-C); 1337.62, 1317.78, 1294.63 (N-C); 825.69, 751.13, 688.38 (=C-H); 825.69 (substituent para). Anal. Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.73; H, 4.545; N, 10.606. Found: C, 68.36; H, 4.958; N, 9.461.

1,3-*Bis*(4-bromophenylamino)squarine (**SQG2**) was prepared from *p*-bromoaniline (5 mmol; 0.86 g) using general procedure. Dye was obtained as a yellow solid (0.80 g, 75.67%.), mp. 359 °C. ^{1}H NMR (DMSO−d_6), δ (ppm): 7.5555−7.5775 (d, $J \approx$ 8.08 Hz, 4H, Ar); 7.7422−7.7638 (d, $J \approx$ 8.64 Hz, 4H, Ar); 11.4480 (s, 2H, -NH-). IR (KBr; cm^{-1}): 3060.26, 2965.23 (=C-H); 2774.56, 2741.75, 2644.58 (NH$_2^+$); 1618.99, 1589.15 (C=O); 1547.16 (N-H); 1492.33, 1429.17,1412.46 (C-C); 1334.54, 1310.78, 1280.86 (N-C); 964.57, 940.83, 840.67 (=C-H); 826.24 (substituent para); 512.23 (Br-C). Anal. Calcd. for $C_{16}H_{10}N_2O_2Br_2$: C, 45.50; H, 2.370; N, 6.635. Found: C, 45.18; H, 2.754; N, 6.649.

1,3-*Bis*(4-ethylphenylamino)squarine was prepared from *p*-ethylaniline (**SQG3**) (5 mmol; 0.62 mL) by general procedure. Compounds was obtained as a yellow solid (0.61 g, 76.32%.), mp. 289 °C. ^{1}H NMR (DMSO−d_6), δ (ppm): 1.1729−1.2107 (t, 6H, -CH$_3$); 2.5712−2.6286 (m, 4H, -CH-); 7.1965−7.2175 (d, $J \approx$ 8.4 Hz, 4H, Ar); 7.6723−7.6930 (d, $J \approx$ 8.28 Hz, 4H, Ar); 11.1395 (s, 2H, -NH-). IR (KBr; cm^{-1}): 3065.18, 2964.93 (=C-H); 2777.26, 2751.12, 2648.68 (NH$_2^+$); 1615.03, 1588.77 (C=O); 1549.01 (N-H); 1428.83, 1410.09 (C-C); 1313.66 (N-C); 847.17; 829.15, 763.42, 728.41 (=C-H); 829.15 (substituent para). Anal. Calcd. for $C_{20}H_{20}N_2O_2$: C, 75.00; H, 6.250;

N, 8.750. Found: C, 73.36; H, 6.081; N, 8.438.

1,3-*Bis*(4-ethoxyphenylamino)squarine was (**SQG4**) synthesized using general procedure from *p*-ethoxyaniline (5 mmol; 0.64 mL). Dye was obtained as a yellow solid (0.66 g, 74.47%), mp. 308 °C. ^{1}H NMR (DMSO−d_6), δ (ppm): 1.2905−1.3484 (m, 6H, -CH$_3$); 3.9769−4.0638 (m, 4H, -CH-); 6.9379−6.9476 (d, $J \approx$ 3.88 Hz, 4H, Ar); 7.6760−7.6991 (d, $J \approx$ 9.24 Hz, 4H, Ar); 11.0144 (s, 2H, -NH-). IR (KBr; cm^{-1}): 3069.38, 2976.36 (=C-H); 2779.34, 2753.10, 2655.32 (NH_2^+); 1623.70, 1593.62, 1554.77 (C=O); 1515.44 (N-H); 1435.20 (C-C); 1301.78 (N-C); 895.04, 835.96, 810.75, 762.21 (=C-H); 835.96 (substituent para). Anal. Calcd. for $C_{20}H_{20}N_2O_4$: C, 68.18; H, 5.682; N, 7.955. Found: C, 65.73; H, 6.066; N, 7.334.

1,3-*Bis*(4-chlorophenylamino)squarine (**SQG6**) was prepared using general procedure from *p*-chloroaniline (5 mmol; 0.638 g). Dye was obtained as a green-yellow solid (0.67 g, 80.44%.), mp. 328 °C. IR (KBr; cm^{-1}): 3061.95, 2968.05 (=C-H); 2777.79, 2740.81, 2646.24 (NH_2^+); 1615.50, 1589.25 (C=O); 1548.56 (N-H); 1494.97, 1429.04, 1413.49 (C-C); 1335.19, 1310.93, 1281.98 (N-C); 840.09, 829.40, 802.64, 762.80, 702.63 (=C-H); 829.40 (substituent para); 671.76, 628.69 (Cl-C). Anal. Calcd. for $C_{16}H_{10}N_2O_2Cl_2$: C, 57.66; H, 3.003; N, 8.408. Found: C, 55.13; H, 3.800; N, 7.647.

1,3-*Bis*(4-iodophenylamino)squarine (**SQG7**) was synthesized by general procedure from *p*-iodoaniline (5 mmol; 0.638 g). Dye was prepared as a green-yellow solid (1.01 g, 78.56%), mp. 328 °C. IR (KBr; cm^{-1}): 3055.85, 2960.85 (=C-H); 2739.80, 2654.22 (NH_2^+); 1616.48, 1589.60, 1559.44 (C=O); 1543.16 (N-H); 1489.01, 1429.71, 1411.60 (C-C); 1339.71 (N-C); 849.74, 841.83, 822.22, 795.59, 762.86, 696.92, 668.49 (=C-H); 822.22 (substituent para); 507.43 (I-C). Anal. Calcd. for $C_{16}H_{10}N_2O_2I_2$: C, 37.21; H, 1.938; N, 5.426. Found: C, 37.24; H, 1.965; N, 5.468.

1,3-*Bis*(4-methylphenylamino)squarine (**SQG9**) was prepared from *p*-toluidine (5 mmol; 0.535 g) using general procedure. Dye was obtained as a yellow solid (0.56 g, 77.05%.), mp. 336 °C. IR (KBr; cm^{-1}): 3070.10, 3037.83, 2982.92 (=C-H); 2776.71, 2748.12, 2660.00 (NH_2^+); 1581.56, 1551.18 (C=O); 1516.00 (N-H); 1428.80 (C-C); 1336.36, 1320.96, 1292.49 (N-C); 840.91, 813.08, 795.61, 764.85, 741.14 (=C-H); 813.08 (substituent para). Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.97; H, 5.479; N, 9.589. Found: C, 73.36; H, 5.632; N, 9.444.

1,3-*Bis*(4-hydroxyphenylamino)squarine (**SQK1**) was synthesized from *p*-aminophenol (5 mmol; 0.545 g) follow general procedure. Dye was obtained as a yellow solid (0.42 g, 56.76%), mp. 328 °C. ^{1}H NMR (DMSO−d_6), δ (ppm): 6.7908−6.8126 (d, $J \approx$ 8,72 Hz, 4H, Ar); 7.6358−7.6536 (d, $J \approx$ 7,12 Hz, 4H, Ar); 9.4518 (s, 2H, -OH); 11.0821 (s, 2H, -NH-). IR (KBr; cm^{-1}): 3424.46, (O-H); 3094.80, 2968.70, 2932.08 (=C-H); 1599.27, 1563.37 (C=O); 1515.74 (N-H); 1446.70, 1428.97 (C-C); 1307.73 (N-C); 755,49 (=C-H); 828,13 (substituent para).

2.1.1.1. Synthesis of 1,3-bis(4-nitrophenylamino)squarine (SQG5).

The squarine dye **SQG5** was synthesized by general procedure presented in point 2.1.1 from *p*-nitroaniline (5 mmol; 0.69 g). Additionally after 4 h, further amount of 1-butanol (20 mL) and toluene (10 mL) was added and the reaction mixture was refluxed for 4 h. Reaction mixture was cooled and the solvent removed on a Büchner funnel. The solid dried in room temperature. Dye was obtained as an orange solid (0.57 g, 84.16%), mp. 356 °C. IR (KBr; cm^{-1}): 3078.32, 2993.04, 2968.24 (=C-H); 2651.35 (NH_2^+); 1586.81, 1560.89 (C=O); 1511.76 (N-H); 1407.43 (C-C); 1339.48, 1311.26 (N-C); 847.17; 843.61, 832.37, 808.31, 782.52, 764.52, 750.18, 685.84 (=C-H); 860.75 (substituent para); 1339.48, 1311.26 (N-O). Anal. Calcd. for $C_{16}H_{10}N_4O_6$: C, 54.24; H, 2.825; N, 15.819. Found: C,52.47; H, 3.680; N, 14.677.

2.1.1.2. Synthesis of 1,3-bis(4-nitrophenylamino)squarine (SQG8).

The squarine dye **SQG8** was synthesized by general procedure presented in point 2.1.1. After 1 h of refluxing, sulfanilic acid (5 mmol; 0.865 g) [20] dissolved in boiling water (16 mL) was added to the reaction mixture. The reaction was continued under reflux for additional 2 h. Next, 1-butanol (20 mL) and toluene (10 mL) was added and refluxed for 2 h. Reaction mixture was cooled and the solvent removed on a Büchner funnel. The solid dried in room temperature. Dye was obtained as a light yellow solid (0.66 g, 61.81%), mp. 277 °C. IR (KBr; cm^{-1}): 2648.54 (=C-H); 1670.83, 1631.72, 1602.08 (NH_2^+); 1577.63, 1548.04, 1522.20 (C=O); 1499.71, 1457.66, 1424.02 (N-H); 1499.71, 1457.66, 1424.02 (C-C); 1319.72 (N-C); 882.13, 846.85, 836.52, 829.82, 819.85, 801.96 (=C-H); 836.52 (substituent para); 1034.79, 1009.90, 686.37 (R-SO$_3$H). Anal. Calcd. for $C_{16}H_{12}N_2O_8S_2$: C, 45.28; H, 2.830; N, 6.604. Found: C, 41.30; H, 4.572; N, 7.833.

2.2. Materials

Aniline, *p*-bromoaniline, *p*-ethylaniline, *p*-ethoxyaniline, *p*-chloroaniline, *p*-iodoaniline, *p*-toluidyne, *p*-aminophenol, *p*-nitroaniline, sulfanilic acid, diethyl ether, tetrahydrofuran (THF), acetone, acetonitrile, ethanol, methanol, dimethylsulfoxide (DMSO), distilled water, toluene, 1-butanol, *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (MP) were purchased from Sigma-Aldrich (Poland). All chemicals were of analytical grade.

2.3. Measurements

2.3.1. Nuclear magnetic resonance spectroscopy

The ^{1}H and ^{13}C NMR spectra were recorded used an Ascend III spectrometer operating at 400 MHz, Bruker (USA). Dimethylsulfoxide (DMSO-d_6) was used as a solvent and tetramethylsilane as internal standard.

2.3.2. Fourier transform infrared spectroscopy FTIR

FTIR spectra of obtained dyes were recorded on spectrometer Vector 22 Bruker USA in KBr pellets with frequency range 4000−400 cm^{-1}.

2.3.3. Melting point measurements

Melting points (uncorrected) were determined on the Boeöthius apparatus − PGH Rundfunk, Fernsehen Niederdorf KR, Stollberg/E.

2.3.4. Elemental analysis

The elemental analysis was made with a Vario MACRO 11.45−0000, Elementar Analyser System GmbH (Germany), operating with the software VARIOEL 5.14.4.22.

2.3.5. Spectroscopic measurements

An influence of substituent on absorption spectra and solvatochromic properties of dyes were measurement on a Cary 50 spectrophotometer (Varian) in quartz cuvette 1 cm.

3. Results and discussion

The spectroscopic properties of squarine dyes under study in different solvents are presented in Table 1.

As shown in Fig. 1, the hypsochromic shift of absorption maximum of **SQG5** in different solvents as an effect of increasing polarity of solvents from nonpolar diethyl ether to polar protic solvent, such as methanol and water was observed. The same effect was observed for all other *p*-substituted aniline derivatives.

Table 1
The spectroscopic properties of squaraine dyes in different solvents.

Solvent	λ_{max}(nm) ε (dm^3 cm^{-1} mol^{-1})																			
	Diethyl ether		THF		Acetone		Ethanol		Methanol		1-Methyl-2-pyrrolidinone		Acetonitrile		DMF		DMSO		Water	
Dye																				
SQG1	399	5334	401	6923	398	11263	393	11172	390	10901	386	1873	393	7607	390	3578	398	5580	374	3035
SQG2	415	49478	410	46739	407	39542	402	44776	400	47271	405	30301	402	39542	401	33735	405	36148	342	21673
SQG3	405	60833	405	59690	404	52931	397	61649	394	59298	405	44212	396	50678	401	53584	404	47706	341	29682
SQG4	409	16587	409	40613	407	10930	403	34432	400	35410	410	27727	397	6216	407	34083	408	34292	340	19730
SQG5	470	26860	474	22073	465	48864	470	28685	454	35951	530	22693	487	25241	522	24208	523	24139	312	12879
	519	16391	527	21178															399	13396
SQG6	412	43799	410	41407	409	46191	400	388609	398	40755	403	23950	399	33673	399	28330	404	33114	342	13078
SQG7	418	41320	413	41018	407	23180	404	38347	402	24389	409	16730	399	25850	403	40968	407	40968	349	23532
SQG8	–	–	–	–	374	3310	402	4609	402	4818	410	4902	406	3184	408	8044	408	3729	393	7374
SQG9	406	46420	404	46125	402	22194	397	45507	394	44595	404	34414	395	34763	402	39591	401	39944	352	15601
SQK1	410	41836	410	41603	407	39069	403	40758	398	40117	412	33795	402	38661	408	38049	410	36621	374	7429
	542	3350	558	3991			554	2972	548	2272	554	6846	542	2709	555	6817	556	4865		

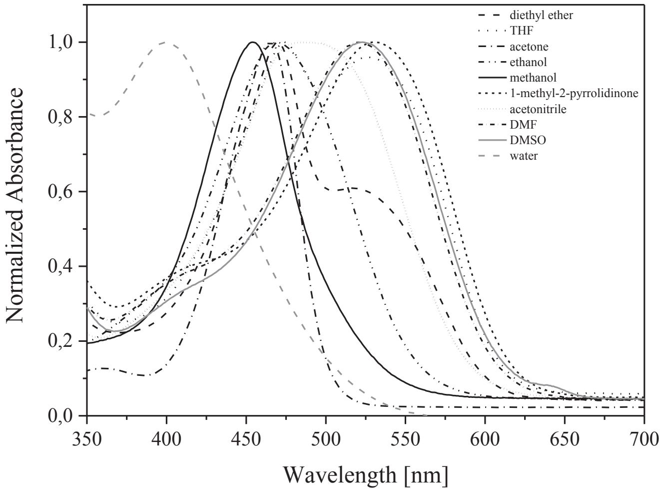

Fig. 1. Normalized absorption spectra of squarine dye (SQG5) in different solvents.

The effect of substituent was also study in different solvents. Generally, the red shift of absorption band is observed for all *p*-substituted aminosquarines in comparison with the dye without any substituent (**SQG1**). The stronger bathochromic effect is caused by strong electron-accepting substituents. For example, the introduction of nitro group into the dye structure leads to shift of absorption band about 70 nm in comparison to the unsubstituted squarine. In the case of the dyes possessing an electron donating group the observed bathochromic shift changes from 6 nm to 10 nm for ethyl and hydroxyl groups, respectively. The absorption spectra of all synthesized dyes in diethyl ether are presented in Fig. 2.

The effect of solvent polarity and hydrogen bonding on sqarylium *p*-aniline derivatives were studied using the linear solvation energy correlation described by Kamlet Taft equation presented below (Eq. (1)) [23]:

$$\nu = \nu_0 + a\alpha + b\beta + s\pi^* \tag{1}$$

where: α is the scale of the solvent hydrogen bond donor acidity, β is the scale of the solvent hydrogen bond basicity, π^* is a

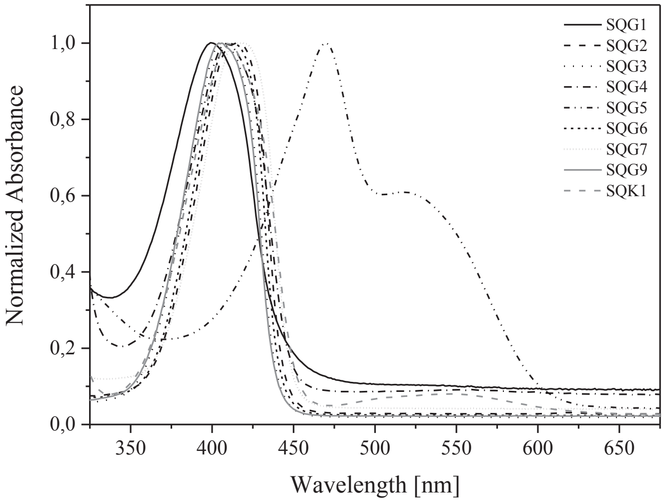

Fig. 2. Normalized absorption spectra of squarine dyes in dimethyl ether.

Table 2
Kamlet-Taft solvent parameters.

Solvent	α	β	π*
Diethyl ether	0	0.47	0.27
Tetrahydrofurane (THF)	0	0.55	0.58
Acetone	0.08	0.43	0.71
Ethanol	0.86	0.75	0.54
Methanol	0.98	0.66	0.6
1-Methy1-2-pyrrolidinone (MP)	0	0.77	0.92
Acetonitryle	0.19	0.4	0.75
Dimethylformamide (DMF)	0	0.96	0.88
Dimethyl sulfoxide (DMSO)	0	0.76	1
Water	1.17	0.47	1.09

Table 4
Hammett substituents constant.

Substituent	σ_p
H	0
Br	0.23
C_2H_5	−0.15
OC_2H_5	−0.24
NO_2	0.78
Cl	0.23
I	0.18
SO_3H	0.35
CH_3	−0.17
OH	−0.37

measure of the solvent dipolarity/polarizability and ν_0 is the regression value of the solute properties in reference solvent cyclohexane. The regression coefficient a, b and s in Eq. (1) measure the relative susceptibility of the solvent dependent of solute property (absorption frequencies) to the indicated solvent parameters. The Kamlet −Taft α, β and π* solvent parameters are listed in Table 2.

The multiple linear regression are used to find correlations of the spectroscopic data of studied squarine dyes for ten selected solvents. The results of multiple regression are listed in Table 3.

The positive sign of coefficient s and a for all squarine dyes without **SQG8** indicates hypsochromic shift with increasing polarizability of solvents. This suggest the stabilization of the ground state relative to the electronically excited state. The negative sign of all coefficients in Kamlet-Taft equation for **SQG8** shows a hypsochromic shift with increasing hydrogen bond acidity of solvents. The percentage contribution of solvatochromic parameters (Table 3) for *p*-aniline derivatives of squarylium dyes with strong electron-withdrawing substituent as a nitro group and strong electro-donating substituent as a hydroxyl group and other electron-withdrawing groups shows that the major contribution of solvatochromism is due to solvent acidity hydrogen bond and are the results of specific solute-solvent interactions. The opposite to other electron-donating groups, the major percentage contribution of solvatochromic parameters are due to solvent dipolarity/polarizability which indicate by non-specific solute-solvent interactions.

The absorption frequencies were correlated by Hammett equation (Eq. (2)) using σ_p substituent constants (Table 4) [24]:

$$\nu = \nu_0 + \rho\sigma_p \qquad (2)$$

where: ρ is a coefficient of sensitivity of the absorption frequencies to substituent effects. The correlation parameters of Hammett equation for all solvent are presented in Table 5.

Electron-donating substituents decrease the π-π* transition energy and the bathochromic shift of absorption maximum are observed. Similar to the electron-withdrawing substituents leads to the bathochromic shifts and are observed with increasing of electron-accepting properties. The correlation between absorption frequency and Hammett substituents constant compared to aminosquarine without any substituent are presented in Fig. 3 for electron-withdrawing group and in Fig. 4 for electron-donating group introduced in para position of aniline.

The positive slope for electron-donating substituents (Fig. 3) and negative slope for electron-withdrawing substituents (Fig. 4) with satisfactory correlation (Table 5) were observed for all studied solvents excluding water were only negative slope were observed

Table 3
Multilinear regression fits and percentage contribution of solvatochromic parameters of Kamlet-Taft equation.

Substituent	ν_0 (10^3 cm^{-1})	a (10^3 cm^{-1})	b (10^3 cm^{-1})	s (10^3 cm^{-1})	R	Standard error	F
		P(α) %	P(β) %	P(π*) %			
H	24.45	0.65	−0.062	1.19	0.85	0.58	5.20
		35.65	24.17	40.18			
Br	23.36	1.83	−2.30	3.55	0.9	0.72	8.83
		36.04	30.24	33.72			
C_2H_5	24.25	1.89	−2.63	2.90	0.89	0.71	8.21
		35.62	26.77	37.60			
OC_2H_5	24.18	1.9	−3.33	3.28	0.89	0.71	8.30
		35.33	24.63	40.04			
NO_2	20.41	3.29	−4.17	2.29	0.96	0.88	24.94
		35.77	30.07	34.15			
Cl	23.43	1.84	−2.10	3.39	0.89	0.70	8.31
		36.14	31.17	32.69			
I	23.48	1.64	−2.36	3.32	0.92	0.77	11.35
		35.84	28.95	35.21			
SO_3H	27.04	−0.077	−2.43	−0.53	0.62	−0.062	0.86
		40.36	29.78	29.86			
CH_3	24.40	1.51	−2.18	2.42	0.92	0.78	11.72
		35.60	26.67	37.74			
OH	24.40	1.13	−1.39	1.23	0.94	0.83	16.07
		36.02	36.95	27.03			

Table 5

Linear regression fits of substituent constants in all solvents of Hammett equation.

Solvent	ν_0	ρ	R	Standard error	F
	V_0^a (10^3 cm^{-1})	ρ^a (10^3 cm^{-1})	R^a	Standard $error^a$	F^a
Diethyl ether	25.13	2.09	0.84	0.45	31.79
	25.21	−4.92	0.92	0.67	53.06
Tetrahydrofuran (THF)	24.93	1.58	0.86	0.30	27.02
	25.41	−4.97	0.81	0.38	23.54
Acetone	25.07	1.57	0.77	0.41	14.73
	25.42	−4.87	0.96	0.44	124.53
Ethanol	25.43	1.88	0.86	0.43	18.77
	25.99	−5.49	0.89	0.32	32.45
Methanol	25.60	1.59	0.73	0.54	8.46
	25.98	−4.70	0.91	0.66	49.67
1-Methyl-2-pyrrolidinone (MP)	25.62	4.39	0.83	0.24	15.24
	26.56	−9.16	0.91	0.47	52.99
Acetonitrile	25.49	1.50	0.91	0.26	31.56
	26.20	−6.68	0.91	0.66	39.62
Dimethylformamide (DMF)	25.49	3.13	0.84	0.66	22.23
	26.59	−8.73	0.91	0.66	40.06
Dimethyl sulfoxide (DMSO)	25.13	2.08	0.83	0.45	20.77
	26.20	−8.16	0.84	0.59	27.40
Water	28.75	−4.69	0.58	1.39	11.31
	28.75	−4.69	0.58	1.39	11.31

[a] The linear correlation for electron-withdrawing substituents.

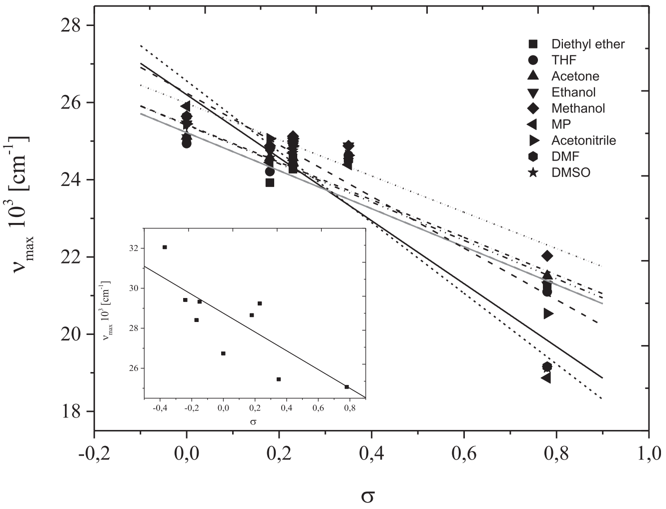

Fig. 3. Correlation between ν_{max} and σ_p for squarine dyes with electron withdrawing group in different solvents.

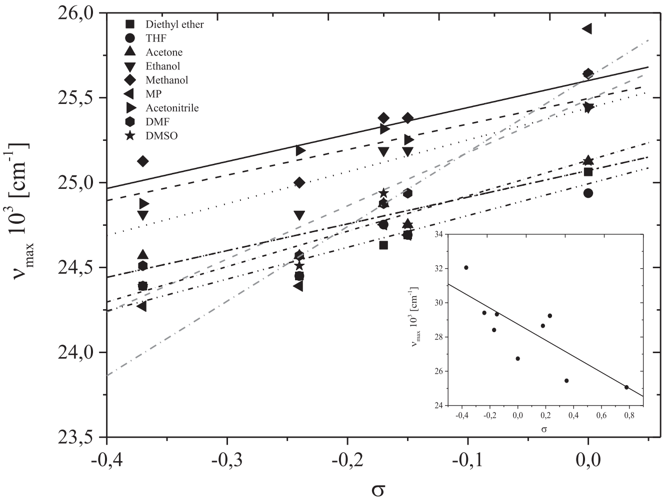

Fig. 4. Correlation between ν_{max} and σ_p for squarine dyes with electron donating group in different solvents, inset correlation between ν_{max} and σ_p for squarine dyes in water.

for all substituents.

4. Conclusions

The series of aniline-based squarine dyes were synthesized and their spectroscopic properties were characterized in ten selected solvents. The effect of solvent show that the electron-donating group presented the major percentage contribution of solvatochromic parameters due to solvent dipolarity/polarizability. Opposite to the strong electron-attracting substituent, strong electro-donating substituent and electron-withdrawing groups which shows the major contribution of solvatochromism due to solvent acidity hydrogen bond donor acidity. The π-π^* transition energy increase with decrease electron-donating constant and electron-withdrawing constant of all substituent due to hydrogen substituents in para position.

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