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Factors that influence the spectroscopic properties of 1,3-bis[*p*-substituted-(phenylamino)]squaraines

Janina Kabatc^{a,*}, Katarzyna Kostrzewska^a, Łukasz Orzeł^b

^a UTP, University of Science and Technology, Faculty of Chemical Technology and Engineering, Seminaryjna 3, 85-326 Bydgoszcz, Poland
^b Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Cracow, Poland

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1. Introduction

Squaraine dyes, first synthesised in the mid-1960s, consist of an oxocyclobutenolate core with aromatic or heterocyclic components at both ends of the molecule [1,2]. Many squaraines, possess polymethine structures with amine and iminium terminals. For this reason, these compounds are occasionally classified as cyanine dyes. 3,4-Dihydroxycyclobut-3-ene-1,2-dione is a core reactant in the synthesis of squaraine dyes [3,4]. Squaric acid is a diacid that exhibits two acidic hydroxyl groups with pKa values of 0.54 and 3.48 as well as two highly polarised carbonyl groups [5]. This unique structure provides not only versatile proton acceptor sites at the carbonyl function, for hydrogen-bonding associations, but also binding sites to metal ions and other compounds [6-8] through the hydroxyl groups. The first synthesis of squaraine dyes was reported by Treibs and Jacob in 1965 [9]. This reaction involved the condensation of 3,4-dihydroxy-3-cyclobutene-1,2-dione with two equivalents of electron-rich aromatics such as α -unsubstituted pyrroles and 1,3,5-trihydroxybenzene under acidic conditions. Since then there have been many squaraine dyes possessing different heterocyclic or aromatic components [7,10,11]. Aniline-

ABSTRACT

The spectroscopic characteristics of a series of ten aminosquaraine dyes that differ in the type of chemical substituent at the *p*-position of the phenyl ring were investigated. The effect of solvent on the properties of the dyes in their ground and excited state is described. The absorption and emission properties, fluorescence lifetime and rate constants for radiative and non-radiative deactivation processes are also presented. The dyes displayed very short fluorescence lifetimes (about 3 ns) and dependence of the radiative deactivation process on the solvent viscosity.

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based squaraines were described for the first time in 1966 by Sprenger and Ziegenbein [12]. The treatment of 3,4dihydroxycyclobut-3-ene-1,2-dione with two molar equivalents of primary or secondary amines avoids the formation of symmetrical squaraines, resulting in a double condensation reaction by the amine [7,13], commonly referred to as aminosquaraines. Amino-squaraines have also been synthesised by the isomerisation of squaric acid 1,2-diamides [7].

Squaraine dyes normally exhibit intense absorption and often fluorescence emission. They have attracted much attention from the viewpoint of technological applications. Generally, the spectroscopic properties of squaraine dyes depend on the chemical structure of the chromophore heterocyclic or aromatic component. Thus, efforts have been made to develop new synthetic methods for constructing squaraine-based chromophores. The search for such chromophores is still relevant due to the important practical applications of squaraines, including xerographic devices utilising the photoconductive properties of squaraine dyes, photovoltaic devices employing the dyes as photosensitisers, dyeing photoinitiating systems employing squaraines also as photosensitisers [14-16] and biolabeling and chemosensory materials for analytical uses. Low band-gap electroconductive materials are available by the polymerisation of squaraine skeletons, as well as supramolecular systems. Furthermore, it should be noted, that these dyes are attaining an increased importance in the field of supramolecular chemistry.





PIĞMĔNTS

^{*} Corresponding author. E-mail address: nina@utp.edu.pl (J. Kabatc).

These dyes have been applied in squaraine-based molecular sensors, self-assembly, in polymeric materials and biological applications [17,18]. The polymers containing squaraine moieties form a new class of low bands gap materials. For example, polyaminosquaraines have been examined as conducting polymers [19]. Moreover, in 2011, the crystal structure and study, from a supramolecular perspective, of other squaraines, e.g. anilinosquaraines, was described by Silva et al. [20].

The aminosquaraine dyes reported here were synthesised by the condensation reaction of squaric acid and a two molar equivalent of (p-substituted)anilines. A characteristic feature of these compounds is the position of the nitrogen atoms in the system of conjugated double bonds. The chemical structures of these aminosquaraine dyes, in particular the type of substituent on the phenyl rings, vary their excited state energetics and the electronic properties [19-22]. For example, as it has been shown by Park et al., slight modification of the squaraine structure by incorporating the aryl amine functional group directly through the nitrogen atom of the amino group to the squarate ring system results in drastically different optical responses [23]. Thus, the objective of these studies was the synthesis of a range of 1,3-aminosquaraine dyes with differing structures, and investigation of their light absorption and fluorescence properties. An understanding of the influence of substituents in the *p*-position of the phenyl rings on the excited state processes is very important in determining the photosensitivity of these squaraine dyes, which is presented also in this article.

2. Experimental

2.1. Materials and general methods

Squaraine dyes were synthesised by reaction of squaric acid with aniline and *p*-substituted anilines, by the general method described in the literature [23]. All reagents and solvents (spectroscopic grade) were purchased from Aldrich (Poland) and used without further purification.

Absorption and emission spectra were recorded at room temperature using an Agilent Technology UV–Vis Cary 60 Spectrophotometer, a Hitachi F-7000 spectrofluorimeter and UV–VIS–NIR Fluorolog 3 Spectrofluorimeter (Horiba Jobin Yvon), respectively. Spectra were recorded in the following solvents: water (H₂O), dimethylsulfoxide (DMSO), acetonitrile (CH₃CN), *N*,*N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (MP), methanol (MeOH), ethanol (EtOH), acetone, tetrahydrofuran (THF) and diethyl ether. The final concentration of dye in solution was 1.0×10^{-5} M. Spectroscopic measurements were performed in the above mentioned solvents containing 20% of 1-methyl-2-pyrrolidinone. For this purpose a suitable amount of dye was dissolved in 1-methyl-2-pyrrolidinone, then 2 mL of the concentrated (ca. 1 mM) stock solution was added to a 10 mL volumetric flask containing spectroscopic grade solvents.

The fluorescence quantum yield for each dye in the solvents was determined as follows. The fluorescence spectrum of a diluted dye solution (A ≈ 0.1 at 366 nm) was recorded by excitation at the maximum of the absorption band of the standard. Dilute Coumarin I ($\Phi=0.64$ [25]) was used as a reference. The fluorescence spectra of Coumarin I was obtained by excitation at 366 nm. The fluorescence quantum yield of each dye (φ_{dye}) was calculated using equation (1):

$$\phi_{dye} = \phi_{ref} \cdot \frac{I_{dye} A_{ref}}{I_{ref} A_{dye}} \cdot \frac{n_{dye}^2}{n_{ref}^2}$$
(1)

where: ϕ_{ref} is the fluorescence quantum yield of the reference, A_{dye}

and A_{ref} are the absorbances of dye and reference at the excitation wavelength, I_{dye} and I_{ref} are the integrated emission intensity for dye and reference, n_{dye} and n_{ref} are the refractive indexes of the solvents used to dissolve dye and reference, respectively.

Fluorescence lifetimes were measured using a single-photon counting UV–VIS–NIR Fluorolog 3 Spectrofluorimeter (Horiba Jobin Yvon). The apparatus utilises, for excitation, a picosecond diode laser generating pulses of about 55 ps at 370 nm. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals with a resolution of few picoseconds possible. Dyes were studied at a concentration able to provide the equivalent absorbance at 370 nm (0.2 in the 10 mm cell) to be obtained. Fluorescence decay was fitted to two exponentials.

3. Results and discussion

Ten aminosquaraines with structures presented in Fig. 1 were studied and have been described here.

The general procedure of synthesis of aminosquaraines was based on the condensation reaction of squaric acid with *p*-substituted aniline derivatives in a mixture of 1-butanol and toluene described in details by Part et al. [23].

The aminosquaraine dyes studied belong to a class of symmetric D–A–D (donor–acceptor–donor) compounds, and differ in the type of substituent in the *p*-position of the phenyl ring. The D–A–D arrangement of each dye molecule has an interesting effect on the formation of intramolecular charge-transfer states. Studies by Kamat et al. [21] on the photochemistry of 1,3-bis[4-(dimethylamino)phenyl]squaraine, and associated quantum chemical calculations, may suggest that 1,3-bis[*p*-substituted(phenylamino)] squaraines are highly polarised, with the *p*-substituted-phenyl-imino moiety being an electron donor (D) and the central C₄O₂ unit being an electron.

It is well known that the properties of ground and excited state compounds depend on the properties of the surrounding solvent. The molecules of a solvent may interact (electrostatic interactions, hydrogen bonding associations, Van der Waal interactions, etc.) with molecules of dissolved compounds. It is also well known that squaraines form a solute—solvent complex in organic solvents; the equilibrium constant of which is dependent on the D–A–D charge-transfer character of the particular squaraine [21]. Therefore, the effects of physicochemical properties of solvent on the properties of each aminosquaraine compound shown in Fig. 1, in its ground and excited state, were studied. The characteristic spectroscopic properties of each aminosquaraine dyes in a few solvents were also studied. The solvents used differed in both polarity and viscosity.

The absorption and emission spectra of the dyes under investigation in acetonitrile are shown in Figs. 2 and 3.

The spectral characteristics of the aminosquaraine dyes are summarised in Table 1.

The aminosquaraines under investigation have intense, sharp absorption bands in the visible region with absorption maxima ranging from 340 nm to 530 nm, and molar extinction coefficients varying from 0.16×10^4 M⁻¹ cm⁻¹ to 11.3×10^4 M⁻¹ cm⁻¹. These molar extinction coefficients are low in comparison with most other squaraine dyes, but are still moderate to high in comparison with simple azo dyes. The position of the absorption band maximum and value of molar extinction coefficient for each dye depends on the dye structure and properties of solvent used. The majority of all aminosquaraine dyes tested, show an intensive yellow colour in all solvents used, with the exception of dye **SQ5**, which possesses a strong electron-withdrawing nitrogen group in the *p*-position of the phenyl rings. The absorption band of **SQ5** is red-shift in comparison to the other dyes studied (see data in



Fig. 1. The chemical structures of 1,3-bis-[p-substituted(phenylamino)]squaraines.



Fig. 2. Absorption spectra of aminosquaraine dyes in acetonitrile.

Table 1).

It should be noted that in solution aminosquaraine dyes exist in two zwitterionic resonance forms. These compounds may also undergo deprotonation, giving monoanion and/or dianions. The deprotonation of the dye strongly depends on the type of substituent in the *p*-positions of the phenyl rings. Introduction of electronwithdrawing groups resulted in mono- or dianion formation. The aminosquaraine dyes without electron-withdrawing substituents exist as zwitterionic forms. It should also be noted that the monoanion of aminosquaraines possess a broader absorption band, in comparison with the zwitterionic form. Therefore, the



Fig. 3. Fluorescence spectra of squaraine dyes in acetonitrile, $\lambda_{\rm EX}$ 380 nm and 490 nm for SQ5.

spectroscopic characteristics of dye **SQ5**, which possesses the strong electron-withdrawing substituent (NO₂) in the phenyl rings, are somewhat different. Deprotonation to the monoanion is much easier, and in some solvents (DMF for example) may occur to some extent without the addition of any base [23], because the solvent has sufficient Lewis basicity. Fig. 4 shows the effect that the Lewis acidity/basicity parameters of the solvents on the electronic absorption spectra of **SQ5**.

From the data presented in Fig. 4, and in Table 2, it can be seen that a solution of **SQ5** in a Lewis base solvent leads to the

Table 1 Spectral characteristics of 1,3-bis-[p-substituted(phenylamino)]squaraines.

	Solvent										
	H ₂ O	DMSO	MeCN	DMF	MP	MeOH	EtOH	Acetone	THF	Ether	
	-										
SQ1											
λ_{ab} [nm]	374	378	390	393	393	390	393	398	401	400	
$\epsilon [10^4 \text{ M}^{-1} \text{cm}^{-1}]$	0.304	0.555	0.36	0.76	0.19	11.0	11.2	11.3	0.69	0.53	
λ _{fl} [nm]	504	504	496	502	495	498	492	490	477	484	
$FWHM_{fl}$ [cm ⁻¹]	13729	5857	7082	4179	4831	7297	7684	7554	14353	8853	
Stokes shift [cm ⁻¹]	6900	6614	5480	5525	5243	5561	5120	4717	3973	4339	
$\phi_{e} [\times 10^4]$	43	11.0	54	28.0	46.0	51.0	67	80	10.0	74	
ψ_{11} [\times 10] k [10 ⁶ s ⁻¹]	0.167	0.448	0.208	1 088	1 708	1 978	0.26	0.31	0.402	0.287	
$K_r [10 \ S]$	2,950	0.440	0.208	2.005	1.750	1.970	0.20	0.51	0.402	0.287	
K _{nr} [10 ⁻ S ⁻]	3.859	3.830	3.838	3.805	3.843	3.841	3.838	3.838	3.857	3.838	
SQ2											
λ_{ab} [nm]	398	405	402	401	405	400	402	407	410	415	
$\epsilon [10^4 \text{ M}^{-1} \text{cm}^{-1}]$	0.558	3.615	3.954	3.374	3.03	4.727	4.477	3.954	4.674	4.948	
λ _{fl} [nm]	506	508	508	477	490	505	511	477	522	520	
$FWHM_{fl}$ [cm ⁻¹]	3547	7112	8527	7455	7661	8673	8159	9186	7600	7411	
Stokes shift [cm ⁻¹]	5363	5006	5190	3973	4283	5198	5306	3605	5233	4865	
$\phi_{0} [\times 10^{4}]$	7 62	7 69	934	677	34 46	27.09	30 32	20.61	11 39	5 57	
$k [10^6 s^{-1}]$	0.283	0.286	0 347	0.252	0 1 2 8	0 101	0 113	0.766	0 424	0.207	
$k [10^8 c^{-1}]$	2 714	2 714	2 712	2 715	2 704	2 707	2 706	2 710	2 712	2 715	
K _{nr} [10 S]	5./14	5.714	5./15	5.715	3.704	3.707	5.700	5.710	5.715	5.715	
SUS	2.41	40.4	200	401	405	204	207	10.1	405	405	
Λ_{ab} [nm]	341	404	396	401	405	394	397	404	405	405	
ε [10* M ⁻ 'cm ⁻ ']	2.968	4.771	5.068	5.358	4.421	5.93	6.165	5.293	5.969	6.083	
λ _{fl} [nm]	488	508	493	499	499	492	495	487	499	497	
FWHM _{fl} [cm ⁻¹]	4821	5928	8408	7107	6548	8568	7894	-	7475	7531	
Stokes shift [cm ⁻¹]	8834	5067	4969	4898	4651	5056	4987	4219	4651	4570	
$\phi_{\rm fl}$ [$\times 10^4$]	15.41	7.015	26.21	27.77	34.08	31.69	7.28	24.42	8.41	6.63	
$k_{\rm r} [10^6 {\rm s}^{-1}]$	0.863	0 3 9 3	1 468	1 556	1 909	1 775	0 408	1 368	0 471	0 371	
$k_{rr} [10^8 \text{ s}^{-1}]$	5 594	5 598	5 588	5 587	5 583	5 584	5 598	5 588	5 597	5 598	
604	5.554	5.550	5.500	5.507	5.505	5.504	5.550	5.500	5.557	5.550	
	240	409	407	207	410	400	402	407	400	400	
Λ_{ab} [1111]	340	408	407	397	410	400	403	407	409	409	
ε[10·M·cm·]	1.973	3.429	3.408	0.622	2.772	3.541	3.443	1.093	4.061	1.659	
λ _{fl} [nm]	499	499	495	498	495	497	497	482	497	490	
FWHM _{fl} [cm ⁻¹]	4787	6123	4495	6345	6076	5991	5955	4219	6481	6729	
Stokes shift [cm ⁻¹]	9372	4470	4368	5109	4188	4879	4639	3823	4329	4042	
$\phi_{\rm fl}$ [$\times 10^4$]	11.43	21.84	38.69	7.84	35.43	33.39	48.11	65.82	10.47	9.21	
$k_r [10^6 s^{-1}]$	1.358	2.593	4.595	0.932	4.208	3.966	5.714	7.818	1.244	1.094	
$k_{\rm pr} [10^8 {\rm s}^{-1}]$	11.863	11.850	11.831	11.867	11.834	11.837	11.819	11.798	11.864	1.866	
S05											
λ. [nm]	300	523	487	522	530	454	470	465	474	470	
$a [10^4 M^{-1} cm^{-1}]$	1 2 2 0	2 414	2 5 2 4	2 421	2,260	2 5 0 5	2,860	405	2 207	2,696	
	1.555	2.414	2.324	2.421	2.209	5.555	2.809	4.000	2.207	2.080	
$\Lambda_{\rm fl}$ [1111]	452	—	371	302	021	2510	545	330	1201	524	
FVVHIVI _{fl} [Cm ⁻¹]	4253	_	1669	-	2755	3513	-	-	1291	1226	
Stokes shift [cm ⁻¹]	2939	_	3021	1363	2765	2647	2928	2849	2300	2193	
$\phi_{\rm fl} [\times 10^4]$	0.971	3.09	1.65	2.31	1.97	3.36	2.48	1.64	1020.2	465.6	
$k_r [10^6 s^{-1}]$	17.784	56.672	30.286	42.279	36.127	61.464	45.449	29.996	18686	8528.4	
$k_{nr} [10^8 s^{-1}]$	1831.5	1831.1	1831.4	1831.2	1831.3	1831.1	1831.2	1831.4	1644.8	1746.4	
SQ6											
λ_{ab} [nm]	342	404	399	399	403	398	400	409	410	412	
$\epsilon [10^4 \text{ M}^{-1} \text{cm}^{-1}]$	1.308	3.311	3.367	2.833	2,395	4.076	3.887	4.619	4.141	4.380	
λ _a [nm]	507	515	516	515	510	509	510	476	519	531	
$FWHM_{a}$ [cm ⁻¹]	4505	7223	8680	10700	8783	9065	8307	9650	7812	7594	
Stolves shift $[cm^{-1}]$	4505	F225	5000	10705 EC4E	5206	5005	5202	2441	5122	F 420	
	12.12	3333	101	15.00	3200	15.00	17.00	12.00	14.05	5455	
$\varphi_{\rm fl}$ [× 10]	13.12	8.24	4.91	15.98	32.10	15.00	17.96	12.99	14.95	9.04	
$K_r [10^\circ s^{-1}]$	0.668	0.419	0.250	0.814	1.637	0.764	0.914	0.661	0.761	0.460	
$k_{nr} [10^{6} \text{ s}^{-1}]$	5.085	5.087	5.089	5.083	5.075	5.084	5.083	5.085	5.084	5.087	
SQ7											
λ _{ab} [nm]	349	407	399	403	409	402	404	407	413	418	
$\epsilon [10^4 \text{ M}^{-1} \text{cm}^{-1}]$	2.353	4.097	2.585	4.097	1.673	2.439	3.835	2.318	4.102	4.132	
$\lambda_{\rm fl}$ [nm]	496	500	478	477	477	506	507	499	514	511	
$FWHM_{e}$ [cm ⁻¹]	3811	6369	7498	10484	7590	6930	7365	6068	6955	6845	
Stokes shift $[cm^{-1}]$	8492	4570	4142	3849	3486	5113	5029	4530	4758	4354	
$\phi_a [\times 10^4]$	14 74	8 88	17 80	8 79	34 12	10.27	25 45	13.05	11 40	11 20	
ψ_{11} [\wedge 10] k [106 c - 1]	0.400	0.00	0 442	0.75	1 1 6 0	0.25	20.40	0.447	0.201	0.204	
$\kappa_{\rm f} [10.5^{-1}]$	0.488	0.504	0.442	0.501	1.109	0.552	0.0/2	0.447	0.591	0.384	
$\kappa_{nr} [10^{\circ} \text{ s}^{-1}]$	3.421	3.423	3.421	3.423	3.414	3.422	3.417	3.421	3.422	3.422	
SQ8											
λ _{ab} [nm]	393	408	406	408	410	402	402	374	-	-	
$\epsilon [10^4 \text{ M}^{-1} \text{cm}^{-1}]$	0.737	0.373	0.318	0.804	0.490	0.482	0.461	0.331	_	_	
λ _{fl} [nm]	478	478	475	478	472	475	477	476	_	_	
FWHM _{fl} [cm ⁻¹]	14229	5903	6020	5297	6890	6307	6276	8562	_	_	
Stokes shift [cm ⁻¹]	4525	3589	3578	3589	3204	3823	3911	5730	_	_	
$\phi_{\rm eff} \times 10^4$	10.45	20.42	18 74	1914	34 46	12 44	1619	22.21	_	_	
$k [10^{6} e^{-1}]$	0 271	0 271	0 725	0 666	0.680	1 2	0 442	0.575	_	_	
$\kappa_{\rm f} [10.5]$	0.3/1	0.371	0.723	0.000	0.000	1.224	0.442	0.373	_	—	
K _{nr} [IU S]	3.549	3.340	3.340	3.340	3.541	3.548	3.547	3.345	_	_	

(continued on next page)

Table 1	(continued)
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	Solvent									
	H ₂ O	DMSO	MeCN	DMF	MP	MeOH	EtOH	Acetone	THF	Ether
SQ9										
λ _{ab} [nm]	352	401	395	402	404	394	397	402	404	406
$\epsilon [10^4 \text{M}^{-1} \text{cm}^{-1}]$	1.560	3.994	3.476	3.959	3.441	4.459	4.551	2.219	4.612	4.642
λ _{fl} [nm]	504	497	510	519	517	513	514	520	523	529
FWHM _{fl} [cm ⁻¹]	4780	7095	7984	7228	6818	9224	8719	-	8079	7951
Stokes shift [cm ⁻¹]	8568	4817	5709	5608	5410	5888	5734	5645	5632	5727
ϕ_{fl} [$\times 10^4$]	26.66	7.81	162.9	7.99	32.72	57.26	42.81	8.45	27.32	5.90
k _r [10 ⁶ s ⁻¹]	1.098	0.322	6.712	0.329	1.348	2.359	1.763	1.125	0.348	0.243
k _{nr} [10 ⁸ s ⁻¹]	4.108	4.115	4.052	4.115	4.106	4.096	4.101	4.108	4.116	4.117
SQ10										
λ _{ab} [nm]	374	410	408	402	412	398	403	407	410	410
$\epsilon [10^4 \text{M}^{-1} \text{cm}^{-1}]$	0.743	3.662	3.805	3.866	3.379	4.012	4.076	3.907	4.160	4.184
λ _{fl} [nm]	_	513	513	507	497	520	518	477	513	535
FWHM _{fl} [cm ⁻¹]	_	6215	7572	6820	6385	6921	6595	7554	6514	7560
Stokes shift [cm ⁻¹]	_	4897	5017	5152	4151	5895	5509	3606	4897	5699
$\phi_{\rm fl}$ [$\times 10^4$]	_	9.42	3.22	6.17	38.44	3.65	5.04	13.84	7.45	9.04
$k_r [10^6 s^{-1}]$	0.327	0.383	0.131	0.251	1.564	0.148	0.205	0.563	0.303	0.368
$k_{nr} [10^8 s^{-1}]$	4.066	4.066	4.068	4.067	4.054	4.068	4.067	4.064	4.066	4.066



Fig. 4. Effect of acidity/basicity parameters of solvents on the electronic absorption spectra of 1,3-bis-(4-nitrophenylamino)squaraine.

broadening of the absorption band, in comparison to the absorption band observed in acetone. Solvent basicity of the Lewis bases presented in Fig. 4, determined by Donor Number (DN), equals 29.8, 27.3 and 26.6 for DMSO, MP and DMF respectively. The application of Lewis basic solvents to **SQ5** results in the deprotonation of the aminosquaraine, leading to monoanion formation (Fig. 5) [23,24].

The dyes under investigation show a blue shift in their respective absorption bands with an increase of solvent polarity, and the lowest fluorescence emission in protic solvents (water for example) with each excited state decaying non-radiatively. Basing on the results described by Park et al. it is known, that the strong hydrogen bonding solvents associate with the oxygen lone pair and/or nitrogen lone pair of each dye molecule reduces the magnitude of the intramolecular charge-transfer associations within the dye molecules [23].

Irradiation of a dye with visible light leads to an excited singlet state formation. The dye in its excited state undergoes different deactivation processes. Generally, they are radiative or nonradiative processes. Fluorescence and phosphorescence are radiative processes but internal conversion and intersystem crossing are non-radiative processes. The triplet state of squaraines cannot be

Table 2

Fluorescence lifetimes and fluorescence quantum yields of squaraines studied in 1methyl-2-pyrrolidinone.

Dye	Fluorescence lifetime [ns]							
	τ_1	τ_2	$\varphi_{fl} \; [\; \times \; 10^4]$					
SQ1	2.60	10.39	46					
SQ2	2.69	10.76	34.46					
SQ3	1.79	7.14	34.08					
SQ4	0.84	3.37	35.43					
SQ5	0.59	_	1.97					
SQ6	1.96	7.86	32.16					
SQ7	2.92	11.68	34.13					
SQ8	2.81	11.26	34.46					
SQ9	2.42	9.71	32.72					
SQ10	2.46	9.83	38.44					

directly populated due to the intersystem crossing quantum yields being poor ($\Phi_{ISC} < 0.001$) [25–28]. The excited triplet state of a squaraine dye can only by generated by triplet–triplet sensitisation [21].

The position of the fluorescence emission maxima for the aminosquaraines under investigation depends both on the structure of the dye and the type of solvent used with maxima ranging from 472 nm to 621 nm, respectively for **SQ8** and **SQ5** in MP. It is known from Kamat et al. [21,22] that the emission spectrum consists of three emission bands that arise as a result of free dye, dye–solvent complex, and a twisted excited state resulting from C–N bond rotation. In the present study the spectral resolution is limited, to resolve the emission bands at room temperature. The first emission band corresponds to the sum of emissions from both free dye and dye–solvent complex (Fig. 6). The second emission band in the red region (~470 nm for dye **SQ8** and ~515 nm for dye **SQ6**), is seen as a result of emission of a twisted excited state, resulting from C–N bond rotation (see Fig. 6) [21].

The fluorescence quantum yield of 1,3-bis[*p*-substituted(phenylamino)squaraines is very low and also depends on the dye structure and polarity of solvents. The highest fluorescence quantum yield (given in Table 1) equals 0.102 for **SQ5** in tetrahydrofuran, and the lowest being 0.000097 for **SQ5** in water. These fluorescence quantum yields observed experimentally are slightly less than the reported value for 1,3-bis[4-(dimethylamino)phenyl] squaraine [21,29].

To understand the excited state dynamics, the fluorescence



Fig. 5. The resonance structures and monoanion of 1,3-bis-(4-nitrophenylamino)squaraine, respectively.

decay lifetimes of the dyes under investigation were measured. Fluorescence lifetimes (τ) have been determined by single photon counting techniques. The fluorescence decay function is a double exponential when monitoring the fluorescence decay at 550 nm, as it is shown in Fig. 7.

The fluorescence lifetimes measured for all dyes in MP are summarised in Table 2.

As observed from the data presented in Fig. 7, and Table 2, the fluorescence lifetime for 1,3-bis[*p*-substituted-(phenylamino)] squaraines in MP solution is very short and equals about 3.0 ns. The fluorescence quantum yield correlates very well with fluorescence lifetime for almost all of the dyes studied. In MP the fluorescence quantum yields and fluorescence lifetimes achieved similar values for all dyes, with the exception of **SQ5**. The introduction of a strong electron-withdrawing group (NO₂) to the aminosquaraine molecule resulted in about 5 times lower fluorescence lifetime and about 15 times decrease in fluorescence quantum yield, in comparison to the other dyes studied. This suggests that the chemical substituent changes bring instability for the excited state of **SQ5**.

With reference to studies by Law et al. [22], it can be concluded that the longer fluorescence lifetimes may be considered as the lifetime of the first singlet excited state of the most stable conformer of the aminosquaraine dye molecule.

The next investigation covered whether or not the fluorescence quantum yield was sensitive to the solvent.

Inspection of data presented in Table 1 showed that the fluorescence quantum yield increases with decrease of solvent polarity (from water to MeOH and from water to MP for **SQ1**, **SQ3**, **SQ4**, **SQ9** and for **SQ2**, **SQ6**, **SQ7**, **SQ8** and **SQ10**, respectively). The observed



Fig. 6. Sum of emission of both free dye and dye–solvent complex and emission of a twisted excited state resulting from C–N bond rotation, respectively.



Fig. 7. Fluorescence decay curves of aminosquaraine dyes in 1-methyl-2-pyrrolidinone as a solvent, $\lambda_{EX} = 370$ nm, $\lambda_{EM} = 550$ nm. Inset: The raport from measurements.

increase in fluorescence quantum yield could be related to dye structure. The first group of dyes possess -H, -alkyl and -alkoxy groups in the *p*-position of the phenyl ring. The second group included chromophores with electron-withdrawing substituents (-Cl, -I, -Br, $-SO_3H$) or an hydroxyl group. This behaviour was the result of interaction between the polarised dye molecule in excited state and the solvent [30]. In most of the dyes (except **SQ5**), the fluorescence quantum yield achieved the lowest values in very low polarity solvents (e.g. THF and diethyl ether).

Taking into account both the fluorescence lifetime (τ) and fluorescence quantum yield (φ_{fl}) , the rate constants of radiative (k_r) and non-radiative deactivation (k_{nr}) processes have been calculated using eq. (2) and eq. (3).

$$k_r = \frac{\phi_{fl}}{\tau} \tag{2}$$

$$k_{nr} = \frac{\left(1 - \phi_{fl}\right)}{\tau} \tag{3}$$

The values of radiative and non-radiative rate constants are summarised in Table 1.

Apart from **SQ5** (possessing a nitro group), for which the rate constants of radiative and non-radiative deactivation are of the order of 10^8 s^{-1} and 10^{11} s^{-1} respectively, the highest rate constants for radiative and non-radiative processes were found for **SQ4** (i.e. ethoxy group), above 10^6 s^{-1} and $1.18 \times 10^9 \text{ s}^{-1}$ respectively. The rate constants for radiative and non-radiative deactivation for the



Fig. 8. The radiative rate constants as a function of solvent viscosity calculated for dyes **SQ6** and **SQ7**, respectively. Inset: The non-radiative rate constants as a function of solvent viscosity.

remaining aminosquaraines were about two orders of magnitude lower than that observed for **SQ5**.

The rate constant for the radiative process depended on the viscosity of the solvent, as shown in Fig. 8. Alternatively, the rate constant of non-radiative deactivation does not depend on the viscosity of the solvent.

It can therefore be concluded that the electronic structure of the fluorescence state is sensitive to the environmental perturbation induced by the solvent. Inspection of Fig. 8 suggests that the value of radiative rate constant increases with an increase in the viscosity of the solvent. In the deactivation process of the excited singlet state, the radiative relaxation process dominates, although in addition to this process, the intramolecular rearrangements, for example solvation phenomena as well as other specific kinds of solute–solvents interactions, might also play a role [30,31].

Furthermore, an excited singlet state may be self-quenched or quenched by other molecule in a bimolecular reaction. A diffusion-controlled self-quenching process has been observed for several dyes [1,2,21]. Such a quenching process is less significant ($k \leq 10^8 \ M^{-1} \ s^{-1}$) in the case of the aminosquaraine dyes.

4. Conclusions

The introduction of strong electron-withdrawing groups in the *p*-position of the phenyl ring (for example: nitro) of 1,3bis(phenylamino)squaraines results in a colour change from yellow to red. The excited singlet state of aminosquaraines undergoes radiative and non-radiative deactivation processes. The rate constant for the radiative process depends on the viscosity of the solvent. However, viscosity of the solvent does not affect the rate of non-radiative deactivation. Fluorescence lifetime is short and equals about 3 ns. The introduction of a nitro group to the *p*-position of the phenyl ring results in a 5 times decrease of fluorescence lifetime, in comparison to other dyes of the same aminosquaraine series. It was also found that the fluorescence lifetime can be correlated to the fluorescence quantum yields for these dyes in 1methyl-2-pyrrolidinone.

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