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# 1,3-Bis(phenylamino)squaraine – Photophysical and photochemical properties

Janina Kabatc <sup>a, \*</sup>, Katarzyna Kostrzewska <sup>a</sup>, Katarzyna Jurek <sup>a</sup>, Robert Dobosz <sup>a</sup>, Łukasz Orzeł <sup>b</sup>

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

#### A R T I C L E I N F O

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## ABSTRACT

A novel squarylium dye possessing donor– $\pi$ –acceptor structure that features a fixed imine phenyl ring as an electron donor and 3,4-dihydroxycyclobut-3-ene-1,2-dione moiety as an electron acceptor was synthesized. The structure of the dye was elucidated by means of NMR and IR spectroscopy and elemental analysis. The compound was studied using steady-state absorption and emission spectroscopy, as well as the time-resolved spectroscopy. The measurements were carried out in solvents of different polarity. The dye absorbs in the visible light region about 400 nm and emits light with low fluorescence quantum yield, below 1 × 10<sup>-3</sup> M. An increases polarity of solvent results in a blue-shift of absorption band and red-shift of emission band, respectively.

The rate constants of radiative and non-radiative deactivation of excited state depend on the viscosity of solvent used. The bimolecular quenching of excited singlet state of squaraine depends on the rate of diffusion process.

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# 1. Introduction

Squarylium dyes often also called squaraines are derived from quadratic acid (squaric acid). According to IUPAC nomenclature they are derivatives of 1,2-dihydroxycyclobuten-3,4-dione.

There are two types of bis-substituted derivatives of squaric acid: 1,2-bis donor substituted and 1,3-bis donor substituted. The merocyanines belong to the first group are essentially and have no distinctive properties, whereas the second type represents an unique group of chromophore, which is neither a merocyanines nor cyanine and has exceptional light absorption characteristics [1]. The most of very important squarylium dyes possess an arylamine or a heterocyclic moiety as the end electron donating groups. The symmetric D-A-D (donor–acceptor–donor) arrangement of squaraine dyes has an interesting effect on the formation of intramolecular charge-transfer states. Basing on the Kamat's and et al. studies [2] on the photochemistry of bis[4-(dimethylamino)phenyl] squaraine and quantum chemical calculations may be suggested

ute—solvent complex in organic solvents, the equilibrium constant of which is dependent on D–A–D charge-transfer character of the squaraine [2]. The next feature of squaraine is the emission from the three different excited states, e.g. free squaraine, solute—solvent complex, and a twisted excited state as a result of C–C bond rotation [2]. Squaraines belong to so-called photosensitizing dyes, that

that 1,3-bis(aminophenyl)squaraine is polarized, with the phenylimino moiety being an electron donor (D) and the central C<sub>4</sub>O<sub>2</sub> unit

being an electron acceptor. The squaraines also form a sol-

absorb strongly in the visible light region and are very important for various imaging applications and solar energy conversion [2,3].

The dye under study was synthesized by a condensation reaction of squaric acid and aniline. A characteristic feature of this compound is a presence of nitrogen atom in the system of conjugated double bonds. There are not any amine and iminium terminals in dye structure. Form our knowledge, such compounds are very rare described in literature. Therefore, in order to improve the knowledge on the physicochemical properties of squaraines, the synthesis and spectroscopic properties of 1,3-bis(phenylamino) squaraine are described in article.





DUES and PIGMENTS

<sup>\*</sup> Corresponding author. Tel.: +48 52 374 9112; fax: +48 52 374 9005. *E-mail address:* nina@utp.edu.pl (J. Kabatc).

### 2. Experimental

# 2.1. Materials and general methods

All reagents and solvents (spectroscopic grade) were purchased from Aldrich (Poland) and used without further purification.

<sup>1</sup>H spectra was recorded in DMSO- $d_6$  on a Bruker Ascend<sup>TM</sup> spectrometer operating at 400 MHz. Chemical shifts are reported in ppm using tetramethylsilane TMS as an internal standard. Coupling constants (*J*) are given in Hz.

IR spectra were recorded on a Bruker Vector 22 FTIR Spectrophotometer (Germany). Samples were prepared by mixing FTIRgrade KBr (Sigma–Aldrich) with 1% (w/w) of dye, and grinding to a fine powder. Spectra were recorded over the 400–4000 cm<sup>-1</sup> range. Characteristic absorptions are given in cm<sup>-1</sup>.

The elemental analysis was made with a Vario MACRO 11.45-0000, Elemental Analyzer System GmbH (Germany), operating with the software VARIOEL 5.14.4.22.

Melting point was measured on the Boëthius apparatus (type PHMK 05, Germany).

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. The spectra were recorded in following solvents: water (H<sub>2</sub>O), dimethylsulfoxide (DMSO), acetonitrile (CH<sub>3</sub>CN), N,N-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (MP), methanol (MeOH), ethanol (EtOH), acetone, tetrahvdrofuran (THF) and diethyl ether. The final concentration of the dye in the solution was  $1.0 \times 10^{-5}$  M. The spectroscopic measurements were performed in mentioned above solvents containing 10% of 1-methyl-2pyrrolidinone. For this purpose a suitable amount of the dye was dissolved in 1-methyl-2-pyrrolidinone, than 0.1 mL of the concentrated (ca. 1 mM) stock solution was added to a 10 mL volumetric flask containing spectroscopic grade solvents under the study. They were characterized by a static dielectric constant ( $\varepsilon$ ) and a refractive index (n) at 20 °C. The solvent polarity function  $f(\varepsilon,n)$  is given by Eq. (1) [1].

$$f(\varepsilon, n) = \frac{(2n^2 + 1)}{(n^2 + 2)} \cdot \left[ \frac{(\varepsilon - 1)}{(\varepsilon + 2)} - \frac{(n^2 - 1)}{(n^2 + 2)} \right]$$
(1)

The fluorescence quantum yield for the dye in solvents were determined as follows. The fluorescence spectra of a diluted dye solution (A  $\approx 0.1$  at 366 nm) was recorded by excitation at the maximum of absorption band of the standard. Dilute Coumarin I ( $\Phi = 0.64$ ) was used as referene [5]. The fluorescence spectra of Coumarin I was obtained by excitation at 366 nm. The fluorescence quantum yield of dye ( $\phi_{dye}$ ) was calculated using Eq. (2):

$$\phi_{\rm dye} = \phi_{\rm ref} \cdot \frac{I_{\rm dye} A_{\rm ref}}{I_{\rm ref} A_{\rm dye}} \cdot \frac{n_{\rm dye}^2}{n_{\rm ref}^2} \tag{2}$$

where:  $\phi_{\text{ref}}$  is the fluorescence quantum yield of the reference,  $A_{\text{dye}}$  and  $A_{\text{ref}}$  are the absorbance of the dye and reference at the excitation wavelength,  $I_{\text{dye}}$  and  $I_{\text{ref}}$  are the integrated emission intensity for the dye and reference,  $n_{\text{dye}}$  and  $n_{\text{ref}}$  are the refractive indexes of the solvents used for dissolve of dye and reference, respectively.

The fluorescence lifetimes were measured using a single-photon counting system UV–VIS-NIR Fluorolog 3 Spectrofluorimeter (Horiba Jobin Yvon). The apparatus utilizes for the 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. The dye was studied at concentration able to provide equivalent absorbance at 370 nm (0.2 in the 10 mm cell) to be obtained. The fluorescence decay was fitted to two exponentials.

The fluorescence quenching measurements were performed using a single-photon counting system UV–VIS-NIR Fluorolog 3 Spectrofluorimeter (Horiba Jobin Yvon). The apparatus uses a picosecond diode laser (370 nm) generating pulses of about 50 ps for the excitation. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals in the range of single picoseconds possible. The dye was studied at a concentration able to provide equivalent absorbance at 370 nm (0.2 in the 10 mm cell). The rate constant for the quenching of 1,3-bis(phenylamino) squaraine by all quenchers under studies were determined in 1-methyl-2-pyrrolidinone. The concentration of dye was  $2 \times 10^{-5}$  M and that of the quenchers was in the range from  $1 \times 10^{-4}$  M to  $5.0 \times 10^{-3}$  M. The fluorescence quenching at 440 nm was measured in deaerated solution by bubbling with argon.

#### 2.2. Synthesis

1,3-Bis(phenylamino)squaraine was synthesized according with general method: squaric acid (0.290 g, 2.5 mmol) 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, aniline (5 mmol) was added and the reaction mixture refluxed for additional 4 h. The suspension was then cooled to room temperature and the solvent removed on a rotary evaporator. The residue was crystallized from 1-butanol and the solid dried in an oven at 50 °C [1,6].

Dye was obtained as a yellow solid (0.38 g, 59%), mp. 328 °C.

<sup>1</sup>H NMR (DMSO- $d_6$ ),  $\delta$  (ppm): 7.1196–7.1566 (t, 2H, Ar); 7.3625–7.4021 (t, 4H, Ar); 7.7874–7.8073 (d, J = 7.96 Hz, 4H, Ar); 11.2766 (s, 2H, –NH–).

IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3087.87, 3058.58, 2992.99, 2967.42 (=C-H); 2777.99, 2746.84, 2680.45 (NH<sub>2</sub><sup>+</sup>); 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); 1261.90, 1245.62, 1184.03, 1164.73, 1145.56, 1098.39, 1079.20 (C-O); 825.69, 751.13, 688.38 ("oop"); 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, 72.66; H, 4.558; N, 10.561.

## 2.3. Computational details

Gaussian 09 [7] software package was used for calculations. For the optimization of geometry of the ground and first excited

state of the **SQ** dye molecule the B3LYP/6-311++G(d,p) method was used. Frequencies analysis were performer at the same level. All calculations were performed in the gas phase (no intermolecular interactions were considered). For visualization of the surfaces of molecular orbitals the Gabedit software [8] was used.

#### 3. Results and discussion

#### 3.1. Synthesis

Structure and purity of 1,3-bis(phenylamino)squaraine was confirmed by FTIR, <sup>1</sup>H NMR spectroscopy, elemental analysis and thin layer chromatography. The data were found be in good agreement with the structure of dye. The <sup>1</sup>H NMR spectra of dye shows characteristic bands in the region of  $\delta = 1.0-9$  ppm. In the region the signals characteristic for the protons in benzene ring, cyclobut-3-ene-1,2-dione ring, and the imino group are present.

The IR spectra indicates some characteristic bands for the dye obtained. For example, the aromatic stretching vibrations for C–N and C=C bonds were observed in the frequency range from 1295 cm<sup>-1</sup> to 1500 cm<sup>-1</sup> and for C–H in the range from 2967 cm<sup>-1</sup> to 3088 cm<sup>-1</sup>. The stretching vibrations for C=O were observed in the frequency range from 1615 cm<sup>-1</sup> to 1592 cm<sup>-1</sup>.

#### 3.2. Ground state of squarylium dye

The presence of an electron donating end group attached to the squaric acid results in delocalized nature of  $\pi$ -electron system. Fig. 1 presents the surfaces of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) defined by quantum chemical calculations.

Dirk C. et al. used X-ray crystallographic analysis also confirmed the delocalization of  $\pi$ -electrons in squarylium dye structure [9].

In solution squarylium dyes exist in form of two neutral resonance structures. These compounds may also undergo deprotonation giving monoanion or/and dianions. Fig. 2 presents the possible structures of squarylium dye.

The ability to the deprotonation strongly depends on the type of substituent in *p*-position of phenyl ring [1]. The presence of electron-withdrawing group leads to mono- or dianions formation. The squarylium dye under study without any electron-withdrawing group exists only as neutral form. Fig. 3 displays some electronic absorption spectra of 1,3-bis(phenylamino)squaraine recorded at room temperature in solvents of different polarity.

The absorption spectra are broad and have the half-widths of about 3000 cm<sup>-1</sup>. The molar extinction coefficient values are not high and ranging from  $0.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  to  $1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . The absorption band around 400 nm is due to  $\pi \rightarrow \pi^*$  transition. The position of absorption band depends on the polarity of solvent.

#### 3.3. Excited state of squarylium dye

The irradiation of a dye with the visible light leads to an excited singlet state formation. The dye in its excited state undergoes different deactivation processes. Generally, they are radiative or non-radiative. The fluorescence and phosphorescence belong to radiative but internal conversion and intersystem crossing are non-radiative processes. An excited singlet state may also be self-quenched or quenched by other molecules in bimolecular reaction. The fluorescence quenching also belongs to non-radiative processes. For other squarylium dyes, it has been already found that the triplet state cannot be directly populated and that the intersystem crossing quantum yields are poor ( $\Phi_{\rm ISC} < 0.001$ ) [2,10–12]. The excited triplet state of squaraine dye can by



Fig. 1. The presentation of structure, HOMO (left) and LUMO (right) orbitals for 1,3bis(phenylamino)squaraine.

generated by triplet—triplet sensitization [2]. It is well known, that properties of ground and excited state compounds depend on the properties of surrounding solvent. The molecules of solvent may interact (electrostatic interaction, hydrogen bonding, Van der Waals interaction, etc.) with molecules of dissolved compound. Therefore, the effect of solvent on the properties of compound in its ground and excited state was studied. The solvents used differ polarity and viscosity. Fig. 4 presents some fluorescence spectra of 1,3-bis(phenylamino)squaraine recorded at room temperature in solvents of different polarity.

The values of half-width of emission band are much higher than that of absorption band. The broadening of emission band may be result of contribution from more than one form of excited state of squarylium dye. The spectroscopic characteristic of 1,3bis(phenylamino)squaraine is presented in Table 1.

As it is seen from data presented in Table 1, the spectroscopic properties of 1,3-bis(phenylamino)squaraine depend on the polarity of solvent used. An increase of solvent polarity leads to blue shift of absorption spectra and red shift of fluorescence band. The reason of effect of solvent polarity on the absorption and emission properties of dye is different energy of solvation process of molecule in its ground state and Franck-Condon excited state. The negative solvatochromism is caused by better stabilization of the ground state by polar solvents in comparison with excited state. The molecular orbitals taking part in intramolecular charge transfer were shown above (see Fig. 1). The highest occupied molecular orbital (HOMO) is dominated by cyclobut-3-ene-1.2-dione moiety with partially negative charge located at the oxygen atom on central four-member ring. The lowest unoccupied molecular orbital (LUMO) is dominated by azomethine groups. The electronic excitation of squarylium dye leads to the displacement of electron density from electron donating part of molecule to an electron accepting part of molecule. Therefore, the excited state is less polar than the ground state, and hence less stabilized by polar solvents. As a result the negative solvatochromism is expected [4]. The negative solvatochromism observed confirms that the ground state of 1,3-bis(phenylamino)squaraine is more polar than the chargetransfer excited state, and hence lower dipole moment value of the excited state as compared to the ground state is evident [13]. It should be also pointed out that the maximum of emission band in each of the solvents used at room temperature shows a large red shift, more than ca.  $4000 \text{ cm}^{-1}$  with respect to the absorption band. The high value of Stokes shift indicates a significant charge redistribution upon excitation [4,13].

There is observed a linear correlation between spectroscopic properties, e.g. maximum of both absorption and fluorescence bands, Stokes shift and solvent polarity function (f), for dye studied (Fig. 5).

There are several empirical polarity scales which may be applied to investigate the solvatochromism, and different empirical solvent polarity scale, for example: Dimroth-Reichardt's [14], Kamlet-Taft's [15], Lippert-Mataga's [16], Bakhshiev's [17], Kawski-Chamma-Viallet's [18], McRae's and Suppan's scales [19]. The Lippert-Mataga's, Bakhshiev's, Kawski-Chamma-Viallet's, McRae's and Suppan's polarity scales all based on the both the dielectric constant and the refractive index of solvents gave remarkable linear correlations for 1,3-bis(phenylamino)squaraine (Fig. 6). The results obtained confirmed a charge redistribution upon photoexcitation. As anticipated, the largest magnitude of the Stokes shift was observed in the most polar solvents and this variation is indicative of a major change in the dipole moment value referring to a geometry of the excited state different to that of the ground state.

Other characteristic feature of excited state is its lifetime. Fig. 7 shows the fluorescence decay observed for 1,3-bis(phenylamino) squaraine in 1-methyl-2-pyrrolidinone solution.



Resonanse structures of dianion

Fig. 2. Presentation of structures of resonance form, mono- and dianion of neutral squarylium dye.



**Fig. 3.** The electronic absorption spectra of 1,3-bis(phenylamino)squaraine recorded at room temperature in solvents of different polarity.

The fluorescence decay observed was fitted to two exponential curve. The dye exists in two conformers that differ in fluorescence lifetime described by the corresponding components of two exponential models, such as  $\tau_1$  and  $\tau_2$  together with the corresponding amplitudes (**B1** and **B2**). This feature results from interaction of 1,3-bis(phenylamino)squaraine with surrounding solvent. On the basis of fitting of two exponential curve, the fluorescence lifetimes of two conformers were designated. The fluorescence lifetime of conformer appearing predominantly (over 70%) is 2.6 ns. While, the fluorescence lifetime of longer living conformer is equal 10.04 ns.

As noted above, the broadening of emission band in comparison with the absorption band observed for dye under study confirmed the contribution from more than one form of excited state of this dye.

It is well known, that the quantum yield of deactivation of excited state is the sum of quantum yields of all deactivation



**Fig. 4.** Fluorescence spectra of 1,3-bis(phenylamino)squaraine recorded at room temperature in solvents of different polarity,  $\lambda_{EX} = 380$  nm.

processes. As it was mentioned above the fluorescence is one of deactivation processes. Basing on the data presented in Table 1 it is seen that dye under study possess a low fluorescence quantum yield ranging from 0.00043 to 0.0051 which also depends on solvent polarity. The inspection of data presented in Table 1 shows also that the fluorescence quantum yield increases with decrease of solvent polarity (from water to methanol). This behavior is a result of interaction of polarized dye molecule in excited state and solvents [13]. Moreover the lowest fluorescence quantum yield in water, ethanol that belong to polar protic solvents may be result of hydrogen bond formation between dye molecule and surrounding solvent. The hydrogen bonding leads to an additional non-radiative deactivation process.

Taking into account both the fluorescence lifetime ( $\tau$ ) and fluorescence quantum yield ( $\phi_{fl}$ ), the rate constants of radiative ( $k_r$ ) and non-radiative deactivation ( $k_{nr}$ ) processes have been calculated using the Eqs. (3) and (4).

Table 1	
Spectroscopic characteristic of 1,3-bis(phenylamino)squaraine in solvents of different	polarity.

Parameter	Solvent									
	H <sub>2</sub> O	DMSO	MeCN	DMF	MP	MeOH	EtOH	Acetone	THF	Ether
$\lambda_{ab}$ [nm]	374	378	390	393	393	390	393	398	401	400
$\epsilon  [10^4  { m M}^{-1}  { m cm}^{-1}]$	0.304	0.555	0.36	0.76	0.19	11.0	11.2	11.3	0.69	0.53
λ <sub>fl</sub> [nm]	504	504	496	502	495	498	492	490	477	484
FWHM <sub>fl</sub> [cm <sup>-1</sup> ]	13,729	5857	7082	4179	4831	7297	7684	7554	14,353	8853
Stokes shift [cm <sup>-1</sup> ]	6900	6614	5480	5525	5243	5561	5120	4717	3973	4339
$\phi_{\mathrm{fl}}  [ imes 10^4]$	4.3	11.0	5.4	28.0	46.0	51.0	6.7	8.0	10.0	7.4
$k_r [10^6 \text{ s}^{-1}]$	0.167	0.448	0.208	1.088	1.798	1.978	0.26	0.31	0.402	0.287
$k_{nr} [10^8 \text{ s}^{-1}]$	3.859	3.856	3.858	3.805	3.843	3.841	3.858	3.858	3.857	3.858
$f(\varepsilon, n)^{\mathrm{a}}$	0.9136	0.8407	0.8630	0.8357	0.8131	0.8547	0.8126	0.7903	0.5491	0.3766

 $\ensuremath{\mathsf{FWHM}_{\mathsf{fl}}}\xspace$  – the full with at half of fluorescence maximum.

<sup>a</sup> Measured at 20 °C.



**Fig. 5.** Correlation between spectroscopic properties: (maximum of both absorption and fluorescence bands, Stokes shift) and solvent polarity function, f.



**Fig. 6.** Lippert-Mataga's, Bakhshiev's correlations plots for 1,3-bis(phenylamino) squaraine in different polarities solvents. Inset: McRae's and Suppan's solvatochromic correlations plots for dye studied in different polarities solvents.

$$k_r = \frac{\phi_{fl}}{\tau} \tag{3}$$

$$k_{nr} = \frac{\left(1 - \phi_{fl}\right)}{\tau} \tag{4}$$

The values of radiative and non-radiative rate constants are summarized in Table 1. It was found that in polar protic solvents: water, methanol and ethanol the radiative and non-radiative rate constants do not depend on viscosity of solvent. As it is shown in Fig. 8, the radiative rate constant depends on the viscosity of solvent (expect to water, methanol and ethanol).

Therefore one can conclude, that the electronic structure of the fluorescence state is sensitive to the environmental perturbation induced by solvent.

As it was mentioned above, the excited state of dye molecule may be quenched by different molecules in bimolecular reaction. In next step, we study the changes in the fluorescence intensity and fluorescence lifetime under increasing concentration of quencher. The following compounds: tetramethylammonium n-butyltriphenylborate (**B2**), diphenyliodonium chloride (**I1**) and diphenyliodonium hexafluorophosphate (**I2**) were used. The structure of quencher is shown in Fig. 9.

The influence of quencher on the fluorescence intensity and fluorescence lifetime are present in Fig. 10 and Table 2, respectively.

From the comparison of the results obtained for the chromophore alone and chromophore in the presence of quenchers the shortening of the average fluorescence lifetime was observed. The shortening of the fluorescence lifetime is interpreted as a result of interaction of dye with quencher molecule.

An addition of borate salt and iodonium salt results in a significant decrease of the fluorescence intensity and decrease of lifetime of the excited singlet state of dye. Basing on this, it should be noted, that in a presence of suitable quencher the fluorescence state of 1,3bis(phenylamino)squaraine is quenched. The results obtained from fluorescence quenching experiments were analyzed with use the Stern–Volmer relationship Eq. (5).

$$\frac{I}{I_0} = 1 + K_{SV}[Q] = 1 + k_q \tau[Q]$$
(5)

where:  $I_0$  and I are the fluorescence intensities of squarylium dye in absence and presence of quencher, respectively;  $K_{SV}$  is the Stern–Volmer constant, characterized the collision interaction of quencher molecules (Q) with the excited state of fluorophore,  $k_q$  is the quenching rate constant.

From the fluorescence lifetime  $\tau$  and the slope of the linear relationship of Stern–Volmer plot (Fig. 11), one can calculated the  $k_q$  value.



Fig. 7. The fluorescence decay recorded for 1,3-bis(phenylamino)squaraine in 1-methyl-2-pyrrolidinone as a solvent,  $\lambda_{EX}$  370 nm.

From an inspection of the data presented in Fig. 11 it is seen the deviation from linearity of the Stern–Volmer relationship. Taking this into account, one can conclude that fluorescence quenching may occur via dynamic and static mechanism. If the fluorescence quenching occurs by a mixed mechanism (dynamic-static), the quencher molecules interact with the dye molecules in both the ground state and excited state, the Stern–Volmer equation assumes the form:

$$\frac{I}{I_0} = (1 + K_{SV}[Q]) \cdot (1 + K[Q])$$
(6)

and the relationship  $I_0/I = f([Q])$  becomes nonlinear.

From the fluorescence lifetime measurements it is seen, that the decrease of the fluorescence lifetime and changes in the fluorescence intensity of dye under study are observed in whole range of quencher concentration. This confirmed the dynamic mechanism of fluorescence quenching. Therefore, the broken lines for all the three slopes in Fig. 11 can be explained as an evidence of heterogeneity of conjugate formation (namely, two different conjugates are formed with different accessibility for the quenchers). As a result, one part of dye is quenched almost immediately with increase in the quencher concentration. The second, has low quencher accessibility and its fluorescence lifetime is long even at high quencher concentrations.



Fig. 8. The radiative rate constants as a function of viscosity of aprotic solvents calculated for 1,3-bis(phenylamino)squaraine.



Fig. 9. Structures and abbreviation of quenchers studied.



**Fig. 10.** The effect of diphenyliodonium on the fluorescence intensity of 1,3-bis(phenylamino)squaraine in 1-methyl-2-pyrrolidinone as a solvent.

If there is more than one fluorophore, their individual participation should be taken into account. In such a case, the general Stern–Volmer equation assumes form:

$$\frac{I}{I_0} = \sum_{i=1}^n \frac{f_i}{1 + K_{SV}[Q]e^{V[Q]}}$$
(7)

Table 2

Effect of the quencher concentration on the fluorescence lifetime of squarylium dye.

Concentration of	B2	I1	I2
quencher [M]	τ [ns]	τ [s]	τ [ns]
0	8.0552	8.0552	8.0552
$1.0  imes 10^{-4}$	6.6514	7.5734	4.7261
$2.0  imes 10^{-4}$	6.2689	7.2019	4.62
$3.0  imes 10^{-4}$	6.0698	6.9457	4.5713
$4.0  imes 10^{-4}$	5.5764	6.7155	4.5018
$5.0  imes 10^{-4}$	5.5571	6.464	4.4241
$6.0  imes 10^{-4}$	5.3186	6.2186	4.2558
$7.0  imes 10^{-4}$	5.236	5.9575	4.2837
$8.0  imes 10^{-4}$	5.0116	5.7081	4.2115
$9.0  imes 10^{-4}$	4.9441	5.5116	4.1566
$1.0 \times 10^{-3}$	4.9263	5.3816	4.0706
$1.5 \times 10^{-3}$	4.6455	5.0397	3.8678
$2.0  imes 10^{-3}$	4.2855	4.6269	3.6827
$3.0  imes 10^{-3}$	3.7565	3.8739	3.3825
$4.0  imes 10^{-3}$	3.4134	3.3821	3.0513
$5.0 \times 10^{-3}$	3.1794	3.1321	2.9366

 $\lambda_{EX}=370$  nm,  $\lambda_{EM}=440$  nm.

where:  $f_i$  is a fraction of the total fluorescence, v is the constant of static quenching.

The fluorescence quenching rate constant calculated for all quenchers are different for low concentration of quencher than that for higher concentrations. The slopes of Stern-Volmer linear relationship observed (the quenching constant value) are as follows: 622.53 M<sup>-1</sup>, 510.71 M<sup>-1</sup>, 295,05 M<sup>-1</sup>, 284.21 M<sup>-1</sup>, 314.22 M<sup>-1</sup> and 168.60  $M^{-1}$  for **B2**, **I1**, **I2** at concentration below  $1 \times 10^{-3}$  M, and for **B2**, **I1**, **I2** at concentration above  $1 \times 10^{-3}$  M, respectively. Taking into account the fraction of conformer in the total fluorescence (0.71 and 0.29 for  $f_1$  and  $f_2$ , respectively), the rate constants of exited singlet state quenching are equal  $54.87 \times 10^9 M^{-1} s^{-1}$  (**B2**),  $45.01 \times 10^9 M^{-1} s^{-1}$  (**I1**) and  $26.17 \times 10^9 M^{-1} s^{-1}$  (**I2**) for the concentration of quenchers below  $1 \times 10^{-3}$  M. For concentrations of quenchers above  $1 \times 10^{-3}$  M, the rate constants of exited singlet state quenching are equal 10.23  $\times$  10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, 11.31  $\times$  10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> and  $6.7 \times 10^9 \,\text{M}^{-1} \,\text{s}^{-1}$  for **B2**, **I1** and **I2**, respectively. The calculated rate constants are close to the rate constant for diffusion-controlled reaction. The quenching of the excited singlet state of the dye by onium salts is much more efficient in the range of low concentrations (below 1  $\times$  10<sup>-3</sup> M). The rate constant of quenching by diphenyliodonium hexafluorophosphate is lower than that observed for similar salt diphenyliodonium chloride. It is probably due to a higher counter ion in salt I2 than in diphenyliodonium chloride I1, which reduces the mobility of the salt I2.

The influence of borate salt and iodonium salts on the rate of fluorescence decay of the dye suggests that the primary photoreaction occurs between the dye and borate salt and both iodonium salts, respectively. This phenomena may be result of photoinduced electron transfer process occurred between excited dye molecule and quencher in ground state. During photoinduced electrontransfer process squaraine may act as an electron donor or an electron acceptor depending on the electrochemical properties of both dye and quencher [2]. This process may be very useful during application of this dye in dyeing photoinitiating systems for photopolymerization of different monomers.

#### 4. Conclusion

The synthesis and spectroscopic properties of 1,3bis(phenylamino)squaraine were studied in solvents of different polarity. The negative solvatochromism in the absorption spectra and bathochromic shifts of fluorescence spectra were observed with increasing the polarity of solvents. This fact is achieved with



Fig. 11. The Stern–Volmer plots for the quenching of fluorescence of 1,3bis(phenylamino)squaraine by borate salt (B2) and diphenyliodonium salts (I1, I2), respectively.

the occurrence of charge transfer character of the solvent-relaxed emissive state. On the other hand, 1,3-bis(phenylamino)squaraine shows a blue shift in the absorption band and the lowest emission in the protic solvent, water, with its excited state decaying nonradiatively, involving the hydrogen bond interactions. The strong hydrogen bonding solvent forms hydrogen bonds with the oxygen lone pair or/and nitrogen lone pair of dye molecule, which reduces the magnitude of the intramolecular charge transfer within dye molecule. The linear correlations between spectroscopic properties (maximum of absorption band, maximum of fluorescence band, Stokes shift) and different solvent polarity functions were obtained. 1,3-Bis(phenylamino)squaraine in its excited singlet state forms two different conformers varying fluorescence lifetimes. These conformers undergo bimolecular quenching process. The quenching rate constants depend on the structure of quencher is diffusioncontrolled reactions.

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