

# Spectroscopic Study of Solvatochromic Effects in Solution of Amino and Hydroxy Derivatives of Fluorene

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Received January 22, 2003; revised June 18, 2003; accepted June 18, 2003

Spectral properties of fluorene and its amino, hydroxyl and phenyl derivatives have been investigated in polar and non-polar solvents at 293 and 77 K as well as in binary mixtures, e.g. McH/EtOH. The hypsochromic shift of the fluorescence spectrum of the two amino derivatives of fluorene observed in polar solvents has been explained on the basis of its zwitterionic form appearing in the ground state only. The radiative  $k_F$  and non-radiative  $k_{NR}$  and  $k_{ISC}$  rate constants for the compounds under study have been calculated using experimentally determined quantum yields, fluorescence and phosphorescence decay times.

**KEY WORDS:** Fluorene; aminofluorene derivatives; negative solvatochromism.

## INTRODUCTION

The photophysical and photochemical properties of fluorene and its derivatives have been studied extensively in the last decade [1–5]. The reason is the fact that they exhibit several interesting features i.e. they show the twisted intramolecular charge transfer phenomena (TICT) [6], the amino substituents of fluorene form hydrogen bond complexes with protic solvents, or undergo intra/intermolecular complexation and show strong solvatochromaticity [7–11].

The polynitro-9-fluorenol and polynitro-9-fluorenes which have the ability to create charge-transfer tautomers constitute a special groups of fluorene derivatives [12]. They are mostly used to sensitise the photoconductivity of the carbazole molecules dissolved in polymers where they are the most widely known acceptor of the  $\pi$ -electron. Another interesting group of fluorene derivatives are the aromatic amines [8]. They are very good fluorophores and their fluorescence is very sensitive to the environment. Therefore they are often used to probe the characteristics of biomimetic systems and biomembrans [13–16].

In our case hydrogen atoms in the main skeleton of fluorene are substituted by a donor group, e.g. hydroxy (-OH), dimethylamino (-NMe<sub>2</sub>), diethylamino (-NEt<sub>2</sub>) and phenyl (-Ph). In this work as an extension of our earlier work [7] we report the results of steady state and time resolved spectroscopic investigation of those substituted fluorenes in various solutions. For the compounds under studies the fluorescence,  $\Phi_F$ , and phosphorescence,  $\Phi_{Ph}$ , quantum yields, the decay times,  $\tau_F$  and  $\tau_{Ph}$  have been determined and using them the radiative,  $k_F$ , and non-radiative,  $k_{NR}$  and  $k_{ISC}$ , rate constants are calculated.

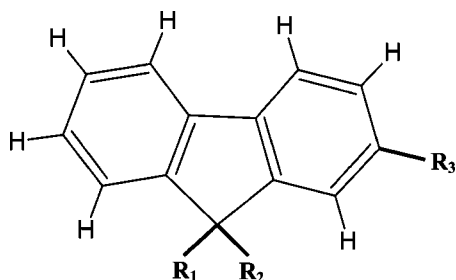
The fluorescence spectra of the amino derivatives obtained in protic polar solutions confirm that in the ground state an open conformer between alcohol molecules and the amino substituent of fluorene ( $\dot{N} \cdots H-O$ ) is created. This conformer shows a negative solvatochromic shift and appears as a zwitterionic form of the solute molecules. These findings have been confirmed by quantum chemical calculations.

## EXPERIMENTAL

The chemical structures of the fluorene derivatives and their abbreviations are shown in Chart I. The Compounds under study were in part obtained from Aldrich Chemical Co. (FL, 9Ph9FOL, 2NEt<sub>2</sub>9FOL) and one of

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Substituents	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Abbreviation
1. Fluorene	H	H	H	FL
2. 9-phenyl-9-fluoreneol	OH	-C <sub>6</sub> H <sub>5</sub>	H	9Ph9FOL
3. 2-dimethylamino-9-fluoreneol	OH	H	-N(CH <sub>3</sub> ) <sub>2</sub>	2NMe <sub>2</sub> FOL
4. 2-diethylamino-9-fluoreneol	OH	H	-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	2NEt <sub>2</sub> 9FOL

Chart I

them (2NMe<sub>2</sub>9FOL) is synthesised [7]. They were used without additional purification. The solvents (supplied by E-Merck Ltd.): cyclohexane (CH), methylcyclohexane (McH), chloroform (ChF), ethyl acetate (EtA), tetrahydrofuran (ThF), methanol (MeOH), ethanol (EtOH), acetonitrile (AcN) were spectroscopic grade. All solvents were checked for purity in the wavelength range of interest, by steady-state and time-resolved spectrofluorometer apparatus. The concentration of solutions was maintained at 10<sup>-4</sup> M through the experiment.

The absorption and the stationary fluorescence spectra at room temperature and 77 K were carried out on Shimadzu UV-2401 PC and RF-5301 spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier and special attachment to obtain phosphorescence spectrum only. Additionally to the neat solution measurement the absorption and emission spectra in the binary mixed solvent at various concentration of EtOH (from 10<sup>-3</sup>–10<sup>-5</sup> M) in McH were carried out. The quantum yields were determined using relative methods [17], where as reference quantum yields ( $\Phi_{FL} = 0, 80$ ) fluorene [18] and 9-phenyl-fluorene ( $\Phi_{FL} = 0.19$ ,  $\Phi_{Ph} = 0.09$ ) were used as a standard [19].

The fluorescence decay times, at room temperature, were determined using the experimental set-up described in [20]. In these measurements the probes were excited with polarised light from a Spectra Physics picosecond laser system consisting of an argon laser-pumped Ti-Sapphire 720–850 nm laser Tsunami. The third harmonic of the Ti-sapphire laser generates picosecond pulses in the region (240–333 nm) at a repetition rate in the range

from 4 MHz to a single shot. The fluorescence light was polarised and observed under the “magic” angle with respect to the polarised exciting beam. The whole light detection system was equipped with a cooled light detector MCP-PMT R3809U-05 coupled with a biased TAC model TC 864 (Tennelec) amplifiner. The data points of the fluorescence decays were fitted by the reference function consisting of the sum of the exponentials:

$$I(t) = \sum_i \alpha_i \exp\left(\frac{-t}{\tau_i}\right), \quad (1)$$

where  $\alpha_i$  and  $\tau_i$  are the pre-exponential coefficient and the decay time of the *i*-th fluorescence component, respectively. Decay curves were both individually and globally analysed by using single, double and triple exponentials. The goodness of the individual fits was judged by the magnitude of  $\chi_R^2 \approx 1$  and the shape of the autocorrelations function and the weighted residuals. The fluorescence decay measurements were carried out at the temperature of 293 K. The phosphorescence decay time was measured on the home made apparatus.

## RESULTS AND DISCUSSION

### Steady State Measurements—Absorption and Emission Spectra

The absorption and emission spectra of fluorene are very precisely described in literature [5,7,18]. Generally the absorption spectrum of fluorene (Fig. 1A) in polar and non-polar solvents consists of three bands in the region 200–310 nm. The first (the strongest) band is in the region 200–230 nm, the second (weaker) in 230–290 nm, the third the weakest possessing vibrational structured is situated in 290–310 nm region. The position and shape of the absorption spectra do not depend on the solvent polarity. A similar absorption spectrum shows the first derivative of fluorene 9Ph9FOL (Fig. 1B) where the three bands appear in the 200–320 nm region. They show a small red shift being determined in different solvents.

For the 2NMe<sub>2</sub>9FOL and 2NEt<sub>2</sub>9FOL compounds the absorption spectra shows big difference in the band position and shape in comparison to that of fluorene (see Fig. 2). They possess in 200–375 nm region only two well resolved bands. The two band, short wavelength with  $\lambda_{max} = 224$  nm and the long wavelength with  $\lambda_{max} = 315$  nm possess comparable molar coefficients with  $\epsilon_M \cong 25,000 \text{ M}^{-1} \text{ cm}^{-1}$  in EtOH.

Figures 1 and 2 display the emission spectra of the respective compounds under study in non-polar (MCH), polar non-protic (ThF) and protic (EtOH) solvents. All

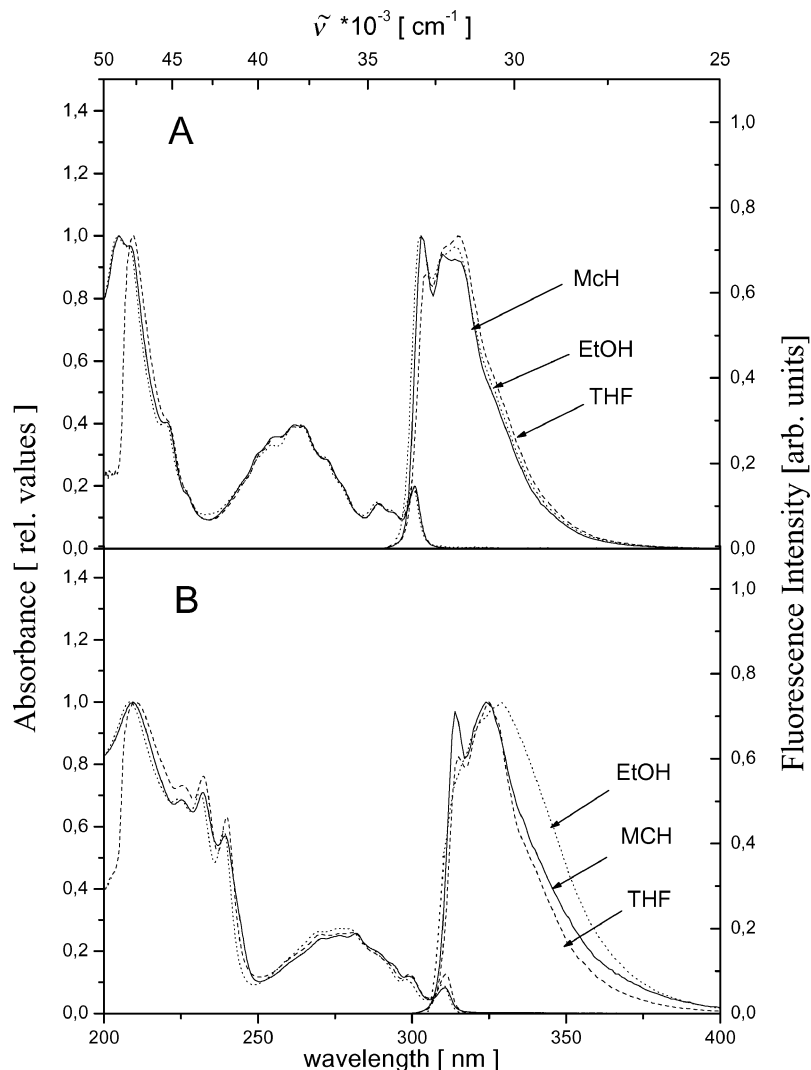


Fig. 1. Absorption and emission spectra of fluorene (A) and 9-phenyl-9-fluorene (B) in different solvents at 293 K.

compounds in the representative solvents possess one fluorescence band only. The emission spectrum of 9Ph9FOL is very similar to that of fluorene and is red shifted about 10 nm in comparison to the parent molecule. Its  $\lambda_{\max}$  depends on the solvent polarity. The half width values of the fluorescence spectra,  $\Delta\tilde{\nu}_{1/2}^{\text{FL}}$ , of FL and 9Ph9FOL are the same and amount to about  $2600\text{ cm}^{-1}$ . The fluorescence spectra of the 2NMe<sub>2</sub>9FOL and 2NEt<sub>2</sub>9FOL are broader and are sensitive to the nature of solvents. They are all shifted to the longer wavelength. The fluorescence band maximum,  $\lambda_{\max}$ , amounts 389 nm and 392 nm for 2NMe<sub>2</sub>9FOL and for 2NEt<sub>2</sub>9FOL respectively.

Table I contains the spectroscopic parameters determined from the absorption and fluorescence spectra of molecules under study. On analysing the collected data,

it follows that the Stokes shift  $\Delta\tilde{\nu}_{\text{ST}}$  (determined as the  $\Delta\tilde{\nu}_{\text{ST}} = \tilde{\nu}_{\max}^{\text{A}} - \tilde{\nu}_{\max}^{\text{FL}}$ ) has different values, for 9Ph9FOL it is comparable with that of fluorene ( $230\text{ cm}^{-1}$  versus  $320\text{ cm}^{-1}$ ) but about 14 times larger value is noted for dimethylamino and diethylamino derivative of fluorene, i.e. (**3** and **4** molecules).

### Substituents and Solvents Effect

When analysing the absorption spectrum of the 9Ph9FOL (Fig. 1B) it can be seen that hydroxyl and phenyl substituent change the short-wavelength band of fluorene at 200–250 nm more than the two longer wavelength bands which are red-shifted by about  $1050\text{ cm}^{-1}$  in McH [5]. In the short wavelength band the oscillation structure is more

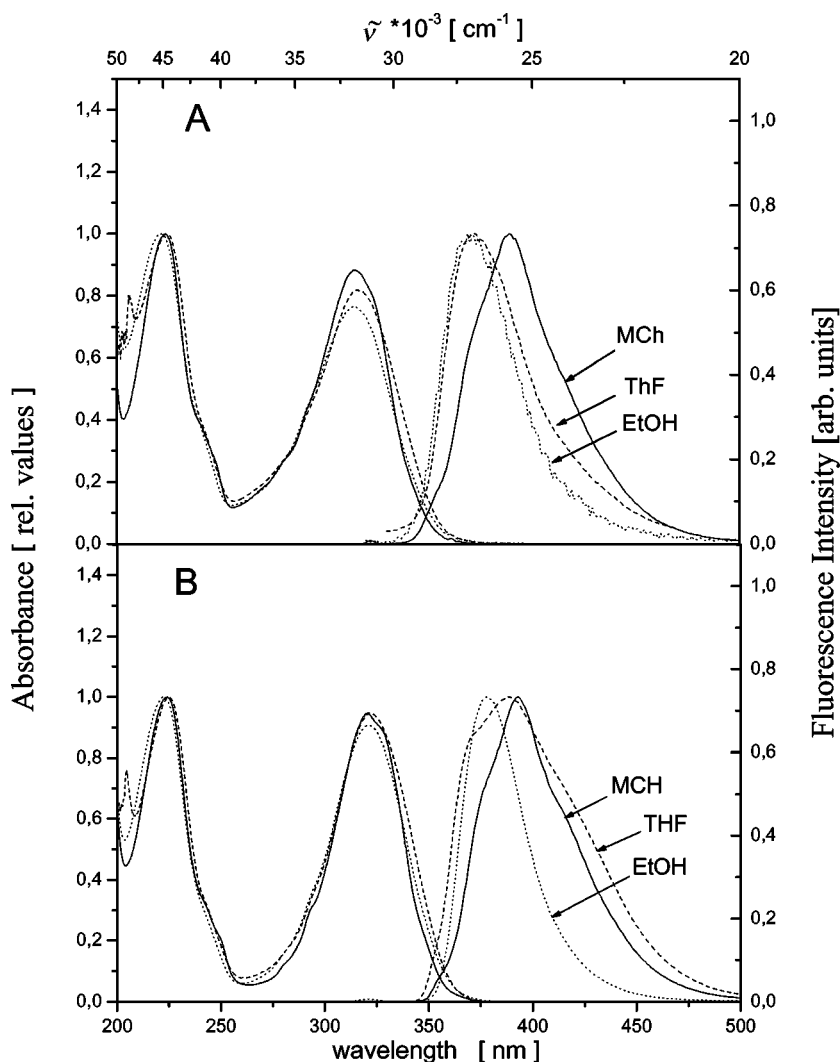


Fig. 2. Absorption and emission spectra of 2-dimethylamino-9-fluorene (A) and 2-diethylamino-9-fluorene (B) in different solvents at 293 K.

pronounced and the band is broadened in comparison to fluorene. It is obvious that the amino group  $-N(\text{Me})_2$  and  $-N(\text{Et})_2$  at position 2 of the parent molecule (along the long axis of the molecule), perturb the long axis transitions of fluorene more than the short axis in the case of molecules **3** and **4**. Fig. 2 demonstrated this behaviour, e.g., in the absorption spectrum of these molecules instead of two bands we observe only one structureless, broad and red shifted band in the longwave part of absorption spectrum of fluorene. The half width of this red shifted band equals to about  $3500$  and  $3400 \text{ cm}^{-1}$  for  $2\text{NMe}_2\text{9FOL}$ ,  $2\text{NEt}_2\text{9FOL}$  in MCh, respectively (Table I). Due to that interaction the long wavelength absorption band of the fluorene derivatives is red-shifted in comparison to the parent molecule (see Table I and [8]).

It is worth noticing that the emission spectra of the two derivatives, by changing the solvent from non-polar to polar and polar-protic solvents, changes the  $\lambda_{\text{max}}$  and  $\Delta\tilde{\nu}_{1/2}^{\text{FL}}$  value. Also, the Stokes shift  $\Delta\tilde{\nu}_{\text{ST}}$  and the destabilisation energy,  $E_{\text{dest}}$  (defined as  $E_{\text{dest}} \cong h\tilde{\nu}_{\text{max}}^{\text{A}} - h\tilde{\nu}_{\text{max}}^{\text{F}}$  [21]) are changed. Analysing respective the data collected in Table I it follows that: for the amino substituted derivatives (**3** and **4**) significantly increase of the  $\Delta\tilde{\nu}_{1/2}^{\text{FL}}$ ,  $\Delta\tilde{\nu}_{\text{ST}}$  and  $E_{\text{dest}}$  values, in comparison to that of fluorene is noted. Changing the solvents from non-polar to polar-protic one, in the case of molecules **3** and **4** the negative solvatochromic effect is observed. This finding can be explained by the fact that the amino substituent in the studied derivatives acts as the proton acceptor for the alcohol molecules.

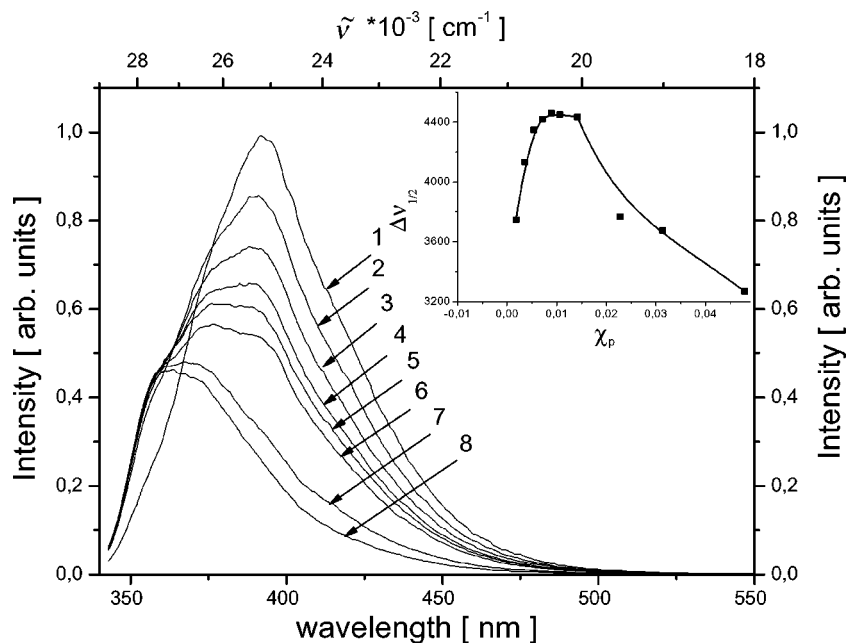
**Table I.** Values of the Long Wavelength Absorption,  $\lambda_{\max}^{\text{Ab}}$  [ $\text{cm}^{-1}$ ] and Fluorescence  $\lambda_{\max}^{\text{FL}}$  [ $\text{cm}^{-1}$ ] Band Maxima, Destabilization Energy,  $E_{\text{dest}}$  (eV), Stokes Shift  $\Delta\tilde{\nu}_{\text{ST}}$  [ $\text{cm}^{-1}$ ] and Full Width at Half Maximum  $\Delta\tilde{\nu}_{1/2}^{\text{FL}}$  [ $\text{cm}^{-1}$ ] of Fluorene and Studied Derivatives in Various Solvent

Solvent	FL	9Ph9FOL	2NMe <sub>2</sub> 9FOL	2NEt <sub>2</sub> 9FOL
<b>McH</b>				
$\lambda_{\max}^{\text{Ab}}$	33,230	32,180	31,780	30,950
$\lambda_{\max}^{\text{FL}}$	33,000	31,860	25,700	25,510
$\Delta\tilde{\nu}_{\text{ST}}$	230	320	6080	5440
$E_{\text{dest}}$	0.03	0.05	0.76	0.72
$\Delta\tilde{\nu}_{1/2}^{\text{FL}}$	2600	2650	3500	3400
<b>ThF</b>				
$\lambda_{\max}^{\text{Ab}}$	33,290	32,180	31,670	31,030
$\lambda_{\max}^{\text{FL}}$	32,820	31,650	26,850	25,830
$\Delta\tilde{\nu}_{\text{ST}}$	470	530	4820	5200
$E_{\text{dest}}$	0.04	0.05	0.59	0.66
$\Delta\tilde{\nu}_{1/2}^{\text{FL}}$	2730	2510	3090	3920
<b>EtOH</b>				
$\lambda_{\max}^{\text{Ab}}$	33,330	32,360	31,830	31,150
$\lambda_{\max}^{\text{FL}}$	33,020	31,640	26,960	26,450
$\Delta\tilde{\nu}_{\text{ST}}$	310	720	4870	4700
$E_{\text{dest}}$	0.04	0.09	0.60	0.58
$\Delta\tilde{\nu}_{1/2}^{\text{FL}}$	2700	4270	2640	2500

Unlike of the rest of the fluorene derivatives for 2NMe<sub>2</sub>9FOL and 2NEt<sub>2</sub>9FOL in EtOH, MeOH and ThF the fluorescence band maximum is blue shifted according to McH and the other non polar solvents (not shown

on Fig. 2). Also, the  $\Delta\tilde{\nu}_{\text{ST}}$ ,  $E_{\text{dest}}$  and  $\Delta\tilde{\nu}_{1/2}^{\text{FL}}$  values (see Table I) are smaller for these derivatives in EtOH than in McH. This unusual fluorescence behaviour has been studied in detail performing additional measurements; e.g., fluorescence spectra measurement in binary mixed solvents, McH/EtOH and EtOH/McH and total emission (fluorescence and phosphorescence) in McH and EtOH obtained at 77 K.

The Fig. 3 shows the emission spectrum of 2NEt<sub>2</sub>9FOL in McH/EtOH mixtures for different molar fraction  $\chi_p$  of EtOH under excitation at  $\lambda_{\text{exc}} = 325$  nm. As we can see, the contents of EtOH in McH increase the fluorescence band position and shape changes. Increasing the EtOH concentration in McH the  $\Delta\tilde{\nu}_{1/2}^{\text{FL}}$  value, first increases the reading of the maximum value and then decreases to the value given for the neat solvent EtOH (see the insert in Fig. 3). This behaviour indicates that the fluorescence spectrum of binary solution consists of two different luminescence centres, e.g., solvates preserving different stoichiometric composition of EtOH and McH in the surrounding of the luminescence molecule. The second obvious observed feature is the hipschrmic shift of the fluorescence band whose value depends on the molar fraction of EtOH. This anomalous shift in protic solvents (MeOH and EtOH) shows that in the S<sub>0</sub> state a specific association is dominated by the weak hydrogen bond. Similar to other amines, the short-wavelength band of the



**Fig. 3.** Fluorescence spectrum of 2-diethylamino-9-fluorenoil in binary mixed solvents (McH/EtOH) at 293 K obtained for different molar fraction  $\chi_p = 0,002$  (1),  $\chi_p = 0,004$  (2),  $\chi_p = 0,005$  (3),  $\chi_p = 0,007$  (4),  $\chi_p = 0,009$  (5),  $\chi_p = 0,02$  (6),  $\chi_p = 0,05$  (7), EtOH(8).

absorption spectrum becomes blue-shifted in EtOH, indicating that the amino group is acting as a proton acceptor in the  $S_0$  state [22]. In the excited state  $S_1$ , the hydrogen bond breaks down and the emission appears from the non-associated molecule. It means that in the ground state we have a highly dipolar complex, alcohol-solute molecule, with almost whole negative charge on the oxygen atom in position 9 of the fluorene skeleton. The non-bonding  $n$  electrons of the nitrogen atom in the amino group take weighing part in the formation of a hydrogen bond. In the  $S_1$  state this weak hydrogen bond is broken and as a result we get a smaller dipole moment in the excited state. In the literature [23] this effect is known as the negative solvatochromism caused by a highly dipolar zwitterionic form of the solute molecule in the ground state and a less dipolar one in the  $S_1$  state.

To confirm the above assumption we calculated the steady dipole moments of the ground  $S_0$  state of **3** and **4** molecules using the standard PM3 and AM1 method (Cache WS 5.04 Program). In order to calculate the  $\mu$  values the necessary optimisation of the geometrical structure for the zwitterionic ( $2NMe_29FOL \cdots EtOH$  or  $2NEt_29FOL \cdots EtOH$ ) and for the free molecule ( $2NMe_29FOL$  and  $2NEt_29FOL$ ) has been employed. Table II shows the computed dipole moments for this two system in vacuum and in a solvent. On analysing data collected in Table II for which the dielectric constant  $\epsilon \approx 24$  (for EtOH) it is evident that for  $2NEt_29FOL \cdots EtOH$  solute possesses  $\mu_{zw}$  value which is almost doubly higher than for free molecule  $\mu_f$ . Such clear evidence is not shown for **3** molecule for which only PM3 calculation gives satisfied results  $\mu_{zw} > \mu_f$ . On the other hand we find out that the partial charge on key atoms is changing. The calculation made with PM3 method shows that on the nitrogen atom the charge decreases after creating hydrogen bond about 25 percent and on the oxygen atom we noted a slight increase of the negative charge. The above results confirm our suspicion that the **3** and **4** molecules

in protic solvents form zwitterionic form in the ground state.

### Emission at 77 K

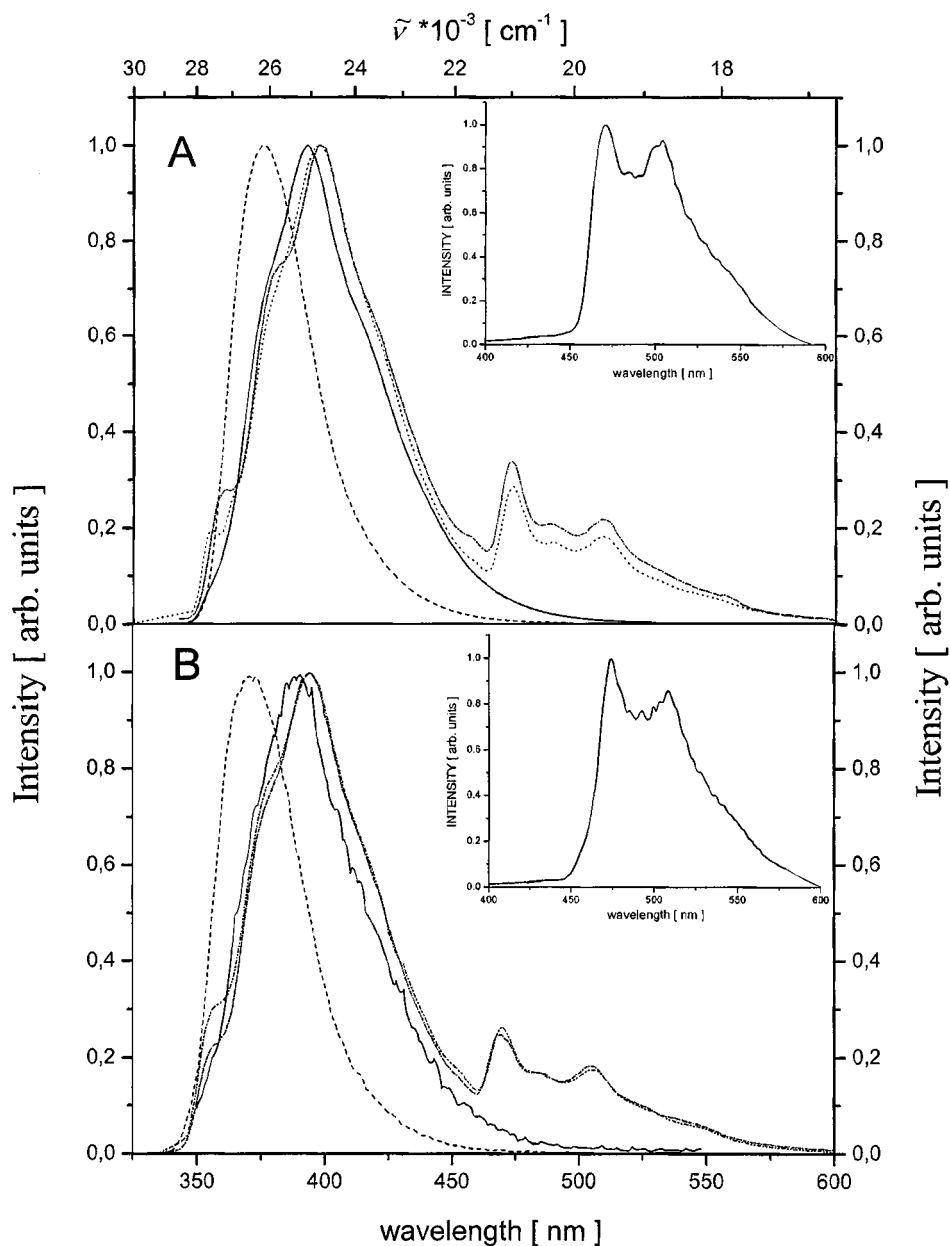
Fig. 4 shows the total luminescence spectra (fluorescence and phosphorescence) for  $2NMe_29FOL$  and  $2NEt_29FOL$  in McH and EtOH at 293 and 77 K. Comparing those obtained at 77 K we see that the fluorescence spectra are similar and follow that obtained in McH at room temperature. A hipsochromic shift and decrease of the  $\Delta\tilde{\nu}_{1/2}^{FL}$  value is noted for alcohol solvents only. This indicates that a zwitterionic form of the two molecules exist only at room temperature (EtOH) in the ground state giving the negative solvatochromic shift. At 77 K the band position of the luminescence spectrum,  $\lambda_{max}$  and  $\Delta\tilde{\nu}_{1/2}^{FL}$  values are the same for these two amino derivatives. These two molecules exhibits structured phosphorescence (see the insert in Fig. 4). The experimentally obtained energy of triplet state  $T_1$  equals 21,110 and 21,270  $cm^{-1}$  for **3** and **4** molecule respectively. When changing the solvent from non-polar McH to polar EtOH there is no drastic changed in position and shape of the phosphorescence spectra. In Table III we placed the determined phosphorescence decay time  $\tau_{ph}$  and calculated phosphorescence quantum yields  $\Phi_{ph}$ . As it follows analysing the data of Table III  $\tau_{ph}$  value equals about 1-s for both molecule amino derivatives indicates that the lowest triplet state has ( $\pi\pi^*$ ) nature. Also, determined quantum yields of phosphorescence show that their values are smaller than for fluorene.

### Fluorescence Decay Time

The fluorescence decay time determined for the molecules under study in EtOH, ThF and McH solvents detecting the fluorescence light at the band maximum. The data obtained are compiled in Table III. The fluorescence decays of compounds **1–4** are well characterised by a single exponential fit with a good  $\chi^2 \approx 0,96–1,17$  and autocorrelation function values. We see that the  $\tau_F$  data depends on the substituent. In all solvents the fluorescence decay time of the fluorene derivatives are shorter from that of the parent molecule. The fluorescence decay time of fluorene obtained by us is in good agreement with the literature value [18]. In the case of 9-hydroxyl-9-phenylfluorene a drasting decrease of  $\tau_F$  value (in comparison) is noted (see Table III) in contrary to that of 9-phenylfluorene ( $\tau_F = 5,1$  ns) [19]. This result suggests that the OH substituent is mainly responsible for the  $\tau_F$  decrease of 9Ph9FOL fluorescence. The amino substituents of 9-hydroxy-9-fluoreneol increase the  $\tau_F$  value by about 3 ns according to FL. The data collected in Table III show

**Table II.** Dipole Moments of the Zwitterionic Form  $\mu_{zw}$  and Free Molecule  $\mu_f$  (in Debye) for **3** and **4**

Method	2NMe <sub>2</sub> 9FOL		2NEt <sub>2</sub> 9FOL	
	$\mu_{zw}$	$\mu_f$	$\mu_{zw}$	$\mu_f$
AM1				
Vacuum	2.20	2.30	4.10	2.30
EtOH	2.70	2.70	4.60	2.70
PM3				
Vacuum	1.90	1.80	3.40	1.90
EtOH	2.30	2.00	3.90	2.20



**Fig. 4.** Luminescence spectrum of 2-diethylamino-9-fluorene (A) and 2-dimethylamino-9-fluorene (B) in McH at 293 K (—) and 77 K (.....) and in EtOH at 293 K (----) and at 77 K (----). The insert consist the pure phosphorescence spectrum obtained on McH.

that the fluorescence decay time for **1**, **3** and **4** molecules increase as the solvent polarity increases whereas the  $\tau_F$  of 9Ph9FOL decreases.

#### Radiative and Radiativeless Rate Constants

Making use of the experimentally determined  $\tau_F$ ,  $\tau_{Ph}$  and  $\Phi_F$ ,  $\Phi_{Ph}$  values of the compounds under study the

radiative ( $k_F$ ) and non-radiative ( $k_{NR}$  and  $k_{ISC}$ ) decay rate constants are calculated using the following forms [19]:

$$k_F = \Phi_F / \tau_F \quad (2)$$

$$k_{NR} = \frac{1}{\tau_F} - k_F \quad (3)$$

**Table III.** Values of Quantum Yields ( $\Phi_F$  and  $\Phi_{Ph}$ ), Fluorescence, and Phosphorescence Decay Time ( $\tau_F$  and  $\tau_{Ph}$ ), the Radiative, ( $k_F$  and  $k_{Ph}$ ), Nonradiative ( $k_{NR}$  and  $k_{ISC}$ ), Rate Constants of the Molecules Under Study in McH and EtOH

Compounds	$\Phi_F$	$\Phi_{Ph}$	$\tau_F$ (ns)	$\tau_{Ph}$ (s)	$k_F$ ( $10^8$ s $^{-1}$ )	$k_{Ph}$ (s $^{-1}$ )	$k_{NR}$ ( $10^8$ s $^{-1}$ )	$k_{ISC}$ ( $10^8$ s $^{-1}$ )
FL								
McH	0.58	0.31	4.48	5.47	1.29	0.13	0.94	0.69
EtOH	0.51	0.15	4.96	5.0*	1.03	0.06	0.99	0.30
9Ph9FOL								
McH	0.08	0.44	0.77	0.69	1.09	0.69	11.89	5.71
EtOH	0.05	0.01	0.10	0.95	1.5	0.01	98.54	0.30
2NMe <sub>2</sub> 9FOL								
McH	0.11	0.05	3.31	1.08	0.32	0.05	2.70	0.15
EtOH	0.03	0.03	3.85	0.89	0.06	0.03	2.53	0.08
2NEt <sub>2</sub> 9FOL								
McH	0.11	0.03	3.34	1.00	0.32	0.03	2.68	0.09
EtOH	0.07	0.06	3.67	1.29	0.18	0.05	2.54	0.16

\*[25]

$$k_{ISC} = k_F \frac{(1 - \Phi_F)}{\Phi_{Ph}} \quad (4)$$

In Table III calculated rate constants are collected which reveal how the environment and molecular structure affect the competition between the various energy dissipation channels. It is obvious that changing solvents from polar EtOH to non polar McH there is no drastic change in the rate constant values noted except constitute molecule **2**. As it follows when analysing the assembled data the non-radiative rate constants follow the inequality  $k_{NR} > k_F$  for all derivatives except fluorene for which  $k_F$  and  $k_{NR}$  are comparable. For amino derivatives of fluorene the  $k_{NR}$  is two order of magnitude higher than for  $k_F$  in EtOH and one order in McH. An explanation of these findings is due to the fact that the flexibility of molecules in the excited states increases the non-radiative decay process. On the other hand the amino substituents of fluorene increase the  $S_1 \rightarrow T_n$  energy gap decreasing the intersystem crossing  $k_{ISC}$  constant. An addition the electron donating dimethylamino group makes  $S_1 \rightarrow T_n$  transition more endothermic which cause the deceleration of the triplet formation [24]. It is interesting to note that for molecule **2** we observed a particular increase of  $k_{ISC}$  in McH in accordance with EtOH and it is followed by connecting with an increase of non-radiative constant  $k_{NR}$  in both solutions in opposition to other molecule.

## CONCLUSIONS

The performed spectroscopic studies of compounds under study confirm that:

- In binary mixed solvents, e.g., McH/EtOH the 2NMe<sub>2</sub>9FOL and 2NEt<sub>2</sub>9FOL molecules show a

negative solvatochromic shift of the fluorescence spectrum. Its appearance is understandable under the assumption that these molecules in alcoholic solvents appear in the zwitterionic form in the ground state  $S_0$  in which they possess a large dipole moment.

- The amino substituents of fluorene cause the bathochromic shift of the absorption and emission spectra and large broadening of the both spectra.
- The hydroxy substituent at 9 position of fluorene (molecule **2**) causes a strong decrease of the quantum yields and fluorescence decay time (about 7 times).
- In all cases except the fluorene, non-radiative process  $k_{NR}$  dominates over the radiative process  $k_F$ .
- Because of the fact that amino derivatives of fluorene exhibit a negative solvatochromism, they can be used as a probe to characterise biological system.

## ACKNOWLEDGMENTS

The authors wish to thank Prof. Józef Heldt for discussion and comments on the manuscript and dr J. Karolczak from Quantum Electronics Laboratory, Faculty of Physics, A. Mickiewicz University at Poznan for his assistance and making the fluorescence lifetime measuring set-up available.

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