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Spectroscopic Studies of Fluorenone Derivatives

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The absorption and steady-state fluorescence spectra of fluorenone, 1-hydroxyfluorenone, and 3-dimethylaminofluorenone have been obtained for various concentrations in a series of non-polar and polar solvents. The substituents (-OH and -$N(CH_3)_2$) as the electron-donating functional groups cause a large shift of the longwave absorption band and Stokes' shift of the monomer- and excimer-fluorescence bands in comparison with fluorenone. The total emission spectrum of 3-dimethylaminoflourenone in polar aprotic solvents exhibits a new band at $\lambda \cong 500$ nm originating form the emission of the twisted intramolecular charge transfer (TICT) isomer. The excited state dipole moments of the emiting species of the molecule studied are determined using the solvatation shift method and calculated values of the ground state dipole moments.

KEY WORDS: Fluorenones; dual fluorescence; excimers; TICT isomers; dipole moments; PACS: 31.70 Dk, 33.50 Dg.

INTRODUCTION

Fluorenone belongs to a group of molecules possessing intriguing spectroscopic and photophysical properties [1–4]. Its appearance originate from the low-lying electronic states influenced by the bridge joining carbonyl group, $\diagdown C = O \diagup$, which introduces a certain compactness of a closed structure to the molecule skeleton. This bridging group induces not only a rigidity and coplanarity of the molecule as a whole but also introduces non-bonding electrons into antibonding π molecular orbitals causing an appearance of n-π^* bands [5–8]. As it follows from [3] the energy difference of the $S_1(n\pi^*)$ and $S_2(\pi\pi^*)$ states of fluorenone is small and depends on the solvent. In polar solvents the electronic states are interchanged as a result of solvent-induced shift. These changes of the character of the lowest singlet state were confirmed by quantum yield, fluorescence decay time measurements and rise time of $T_n \leftarrow T_1(\pi\pi^*)$ absorption determination. Also, it has been shown that the fluorescence spectrum of fluorenone at higher concentrations exhibits, in addition to the monomer band ($\lambda_{max} \cong 350$ nm), a second band at longer wavelength (in the 420–600 nm region) ascribed to fluorenone excimer emission [4].

In this paper we will discuss our results of the steady-state spectroscopic studies of two fluorenone (FL) derivatives, i.e., 1-hydroxyfluorenone (1HOF) and 3-dimethylaminofluorenone (3DMAF) in non-polar solvents (cyclohexane (CH), methylcylohexane (MCH)), polar aprotic solvents (chloroform (Chf), 1,3-dichlorobenzene (m-2CIB), ethyl acetate (EA), 1,2-dichlorobenzene (o-2CIB), acetonitrile (AcN)) and polar protic solvents (methanol (MeOH)).

From the chemical structure analysis of 1HOF and 3DMAF it follows that they are very similar to fluorenone except for the hydroxy and dimethylamino- functional groups replacing fluorenone hydrogens (see Scheme I). On the base of literature studies [7,8,9] one can expect that 1HOF can exhibit excited state intramolecular proton-transfer (ESIPT), whereas the 3DMAF molecule can

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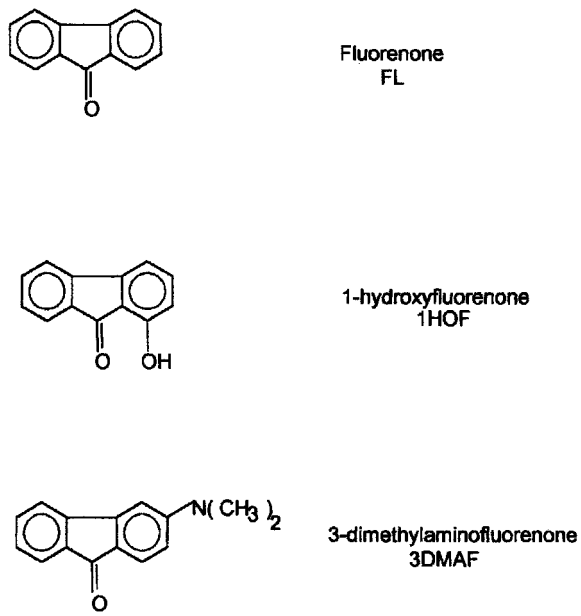

Scheme I. Molecular structure of fluorenone (FL), 1-hydroxyfluorenone (1HOF), and 3-dimethylaminofluorenone (3DMAF).

show the twisted intramolecular charge-transfer (TICT) phenomenon in addition to a photoassociation processes noticed earlier for fluorenone only [2,3].

EXPERIMENTAL

Fluorenone and the two of its derivatives were obtained from Aldrich Chemical Company. Before use, fluorenone was recrystalized from ethanol. The two fluorenone derivatives have been used directly without further purification. The solvents used are of spectroscopic grade and were obtained from E-Merck Ltd. Only the CH and MCH solvents were distilled before used from a sodium potassium amalgam, to ensure they are pure and free of water.

Absorption spectra measurements were carried out using a Shimadzu UV-2401 PC spectrophotometer. The luminescence emission and excitation spectra at room temperature were recorded on a Shimadzu RF-5301 spectrofluorimeter. The radiation was observed perpendicular to the direction of the exciting beam. For the measurements a standard rectangular Suprasil 2, 5 or 10 mm cells were used. The concentration of solutions studied varied in the range $5\cdot10^{-5}$–10^{-3}M. The luminescence spectra have been corrected for the spectral response of the photomultiplier (Hamamatsu R-928) but not for reabsorption.

RESULTS AND DISCUSSION

Figure 1A shows the absorption spectra of the molecules under study obtained in non-polar solvents. The absorption spectra for polar aprotic and polar protic solvents are similar in shape. Each spectrum consists of two distinct bands: a very weak band ($\varepsilon \cong 500$ $M^{-1}cm^{-1}$) in the region 265–310 nm, 265–325 nm and 300–350 nm for FL, 1HOF and 3DMAF, respectively, and a strong band ($\varepsilon \cong 18\ 000$ $M^{-1}cm^{-1}$) with λ_{max} equal to about 257 nm for FL, 260 nm for 1HOF and 280 nm for 3DMAF, respectively. In all solvents used the weak band shows a vibrational structure which is distinctly seen for FL and 1HOF and is very blurred in the spectrum of 3DMAF. The intensity of vibrational peaks, its relative values, depend on the solvent. Also, the ratio of its molar absorption coefficient $\varepsilon\left(\lambda_{max}^{strong}\right)/\varepsilon\left(\lambda_{max}^{weak}\right)$ depend on the solvent. The above ratio in the same solvent has a different value for each molecule, e.g., in MCH 19, 17 and 4 for the FL, 1HOF and 3DMAF molecules, respectively. The decrease of the $\varepsilon\left(\lambda_{max}^{strong}\right)/\varepsilon\left(\lambda_{max}^{weak}\right)$ value with increasing electron-donating strength of the substituent in 1HOF and 3DMAF indicates the charge transfer influence of the $n\pi^*$ long-wave absorption band. A similar change has been found when changing the solvent from a non-polar to a polar one. This findings can be explained in terms of S_1- state character changes from the $n\pi^*$ in MCH to the $\pi\pi^*$ in AcN. Such change for fluorenone has been confirmed in [2,3]. The shape of the absorption spectra of the molecules under study does not depend on the concentration in the range 10^{-3}–10^{-5} M in all solvents used.

Figure 1B shows the fluorescence spectra of the fluorenone and its two derivatives in CH solutions. As can be seen in non-polar solvent, the fluorescence spectrum of the molecules studied possesses two separate bands. The short-wavelength band at $\lambda_{max} \cong 310$ nm for FL, at 322 nm for 1HOF and at 350 nm for 3DMAF is ascribed to the normal fluorescence of the monomer, F_M. The second band at longer wavelength appearing at 460 nm, 480 nm and 570 nm for the FL, 1HOF and 3DMAF molecules, is attributed to the excimer fluorescence, F_{EXC}, as it has been confirmed for fluorenone in [2,3]. The λ_{max} value of the F_M and F_{EXC} fluorescences and its intensities depend on the kind of the fluorenone substituent. For fluorenone in non-polar solvents ($c \cong 10^{-4}$ M) the intensity of normal fluorescence is higher than that of the excimer, i.e., $I_{F_M} > I_{F_{EXC}}$, whereas an opposite dependence is found for 1HOF and 3DMAF molecules (see

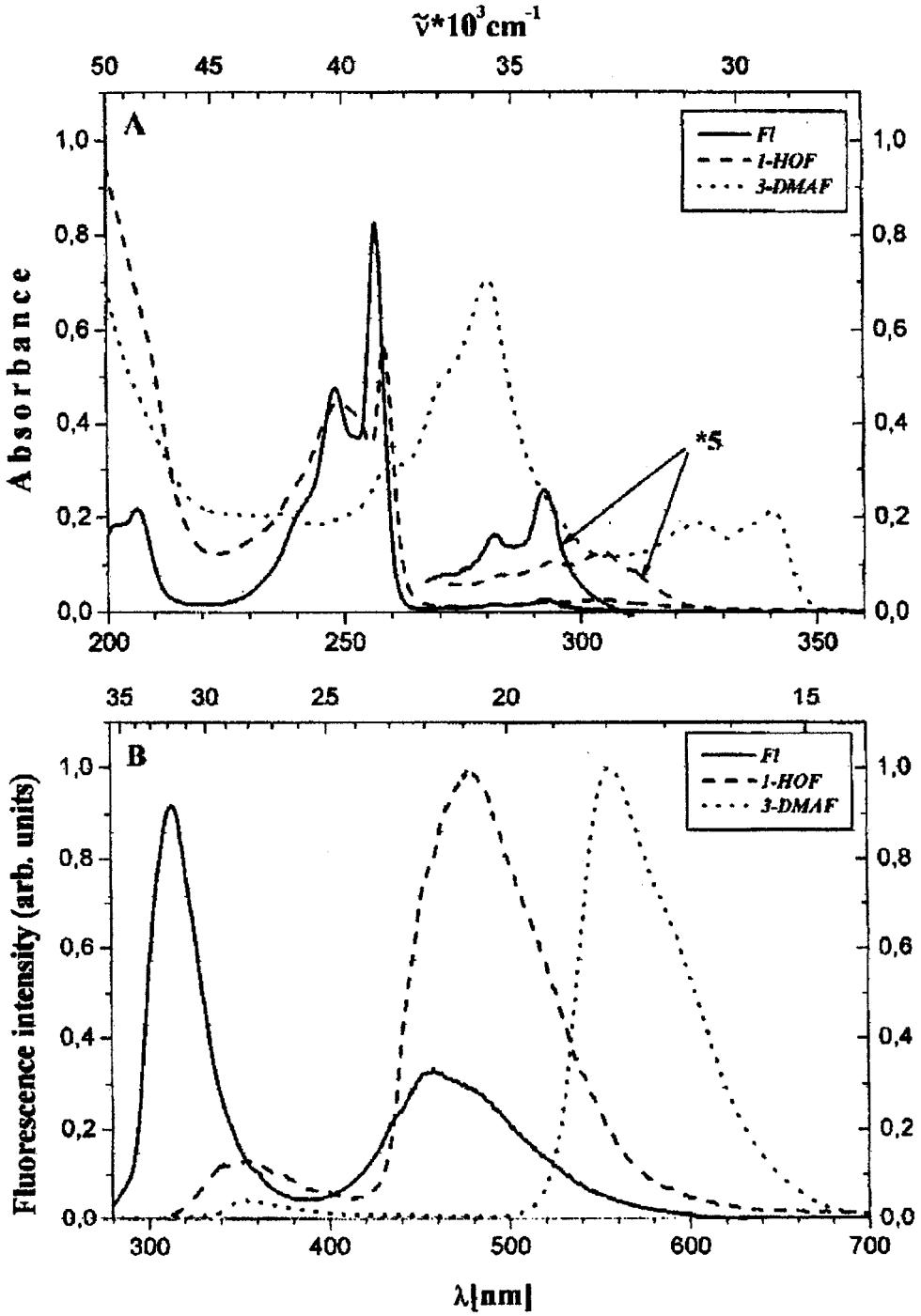

Fig. 1. Absorption (A) and fluorescence (B) spectra of fluorenone (FL), 1-hydroxyfluorenone (1HOF), and 3-dimethylaminofluorenone (3DMAF) in cyclohexane. Concentration, $5 \cdot 10^{-4}$ M.

Fig. 1B). In polar non-protic solvents, the fluorescence spectrum of fluorenone also consists of two bands. Their intensities fulfill the reverse inequality, i.e., $I_{F_M} < I_{F_{EXC}}$, to that found for non-polar solvents.

Table I assembles the λ_{max} values of the longwave absorption band and of the fluorescence bands observed in the total emission spectrum of the molecules under study determined in CH and other solvents used.

Table I. Wavelength Maxima, λ_{max} (in nm and in cm^{-1}), of the Different Fluorescence Emission Modes of FL, 1HOF, and 3DMAF Determined for the Solvents Used

		Fluorenone (FL)			1-Hydroxyfluorenone (1HOF)			3-Dimethylaminofluorenone (3DMAF)			
Solvent	f(n, ε)	$\lambda_A/\tilde{V}_A$	$\lambda_M/\tilde{V}_M$	$\lambda_{EXC}/\tilde{V}_{EXC}$	$\lambda_A/\tilde{V}_A$	$\lambda_M/\tilde{V}_M$	$\lambda_{EXC}/\tilde{V}_{EXC}$	$\lambda_A/\tilde{V}_A$	$\lambda_M/\tilde{V}_M$	$\lambda_{TICT}/\tilde{V}_{TICT}$	$\lambda_{EXC}/\tilde{V}_{EXC}$
Methylcyclohexane	−0.001	293.0	312.0	466.0	322.0	362.5	475.0	340.0	353.0	—	558.5
(MCH)		34,123	32,051	21,459	31,055	27,586	21,052	29,412	28,328	—	17,905
Cyclohexane (CH)	−0.001	292.6	317.5	470.0	315.0	355.0	478.0	340.5	353.0	—	558.0
		34,176	31,496	21,277	31,746	28,169	20,921	29,368	28,328	—	17,953
1,3-Dichlorobenzene	0.124	325.0	368.0	492.0	334.0	368.0	510.0	345.0	371.0	470.0	605.0
(m-2ClB)		30,769	27,174	20,325	29,940	27,174	19,608	28,986	26,954	21,276	16,528
Cloroforem (Chf)	0.157	295.6	355.0	514.2	325.0	—	525.0	305.0	364.0	495.0	612.0
		33,829	28,169	19,450	30,769	—	19,048	32,787	27,472	20,202	16,340
1,2-Dichlorobenzene	0.186	326.6	345.5	492.5	332.0	370.0	508.0	346.0	380.0	500.0	610.0
(o-2ClB)		30,618	28,944	20,305	30,120	27,027	19,685	28,902	26,316	20,000	16,394
Ethyl acetate (EA)	0.201	305.0	318.0	485.0	324.2	—	503.0	340.0	364.0	504.0	610.0
		32,787	31,447	20,619	30,845	—	19,880	29,412	27,472	19,885	16,394
Acetonitrile (AcN)	0.305	294.4	330.0	504.5	330.0	355.0	520.0	340.0	361.0	510.0	—
		33,990	30,303	19,841	30,303	28,169	19,231	29,412	27,692	19,630	—
Methanol (MeOH)	0.309	293.8	320.0	540.0	325.5	370.0	560.0	342.0	380.0	—	—
		34,037	31,250	18,519	30,722	27,027	17,857	29,240	26,316	—	—

Analysing the data assambled in Table I and the spectra shown in Fig. 1 and Fig. 3, it results that the electron-donating substituents -OH and $-N(CH_3)_2$ cause a large shift of the longwave absorption band, i.e., about 3000 cm^{-1} for 1HOF and 4200 cm^{-} for 3DMAF in comparison to that of the parent molecule fluorenone. Whereas the corresponding fluorescence bands are shifted by about 4200 cm^{-1} and 4800 cm^{-1} for the monomer and 500 cm^{-1} and 3500 cm^{-1} for the excimer band of 1HOF and 3DMAF molecules, respectively. The observed large shifts of the absorption and fluorescence band indicate that both functional groups cause an intramoleclar charge transfer to the skeleton of fluorenone.

The fluorescence spectra of 1HOF and 3DMAF in polar non-protic and protic solvents show a more complex structure which depends on the concentration of solute molecules, excitation wavelength and the solvent (see Figs. 2 and 3). Generally, the fluorescence spectrum consist of the normal fluorescence and of the excimer band. But in alcohol solvents one additional peak appears at about 425 nm (see Fig. 2A). Its λ_{max} value, shifted to lower energy by about 3500 cm^{-1}, has been determined as a result of decomposition of the total emission into separate bands of equal half-width. In Figs. 2A and 3 exemplary decomposition into separate bands is given by dashed curves for which $\Delta v_{1/2} = 3400\ cm^{-1}$. As can be seen in Figs. 2A and B, the total emission spectrum of all three molecules in MeOH consists of three bands. Its intensities depend on the solute concentration. Figure 2B shows the total emission spectra of 1HOF obtained for different concentrations as an example. From Fig. 2B follows that an increase of solute concentration causes a decrease of the fluorescence intensities of monomers and H-bond solvates. This dependence is comprehensible if we take into consideration that the formation of excimers and H-bond complexes depend on the solute concentration, which determines the relative participation's of all emitting species [10–13,21–23].

We suppose that for 1HOF alcohol solution the photoinduced excited-state double proto-transfer reaction and H-bond solvation process can undergo. They produce a tautomeric species according to Scheme I. The solvation process, (experimentally and theoretically studied for fluorenone [11]), can take place for 3DMAF as well. In a consequence for the studied molecules it leads to the H-bond complex formation. In this case, as it was shown for 7-azoindole [15], benzanilides [16], acylaminoanthrequinones [17] and 3-hydroxyflavone [8], two emission bands are generally observed. In Fig. 2A and 2B the higher energy emission is due to the species which have not undergone proton transfer (normal monomer fluorescence), while the lower energy emission around $\lambda_{M...H} = 425$ nm is attributed to the H-bond complexes formed according to Scheme I.

Taking into consideration the known energy values of the monomer fluorescence band $\tilde{v}_{max}$ and the H-bond solvate $\tilde{v}_{M...H}$ (see Figs. 2A and B and Table I) the heat of the complex $[^1M^- \ldots HOX]^*$ formation has to be calculated from the relation

$$hc(\tilde{v}_M - \tilde{v}_{M...H}) = -\Delta H^* + E_r \qquad (1)$$

where E_r and ΔH are the activation energy and the heat

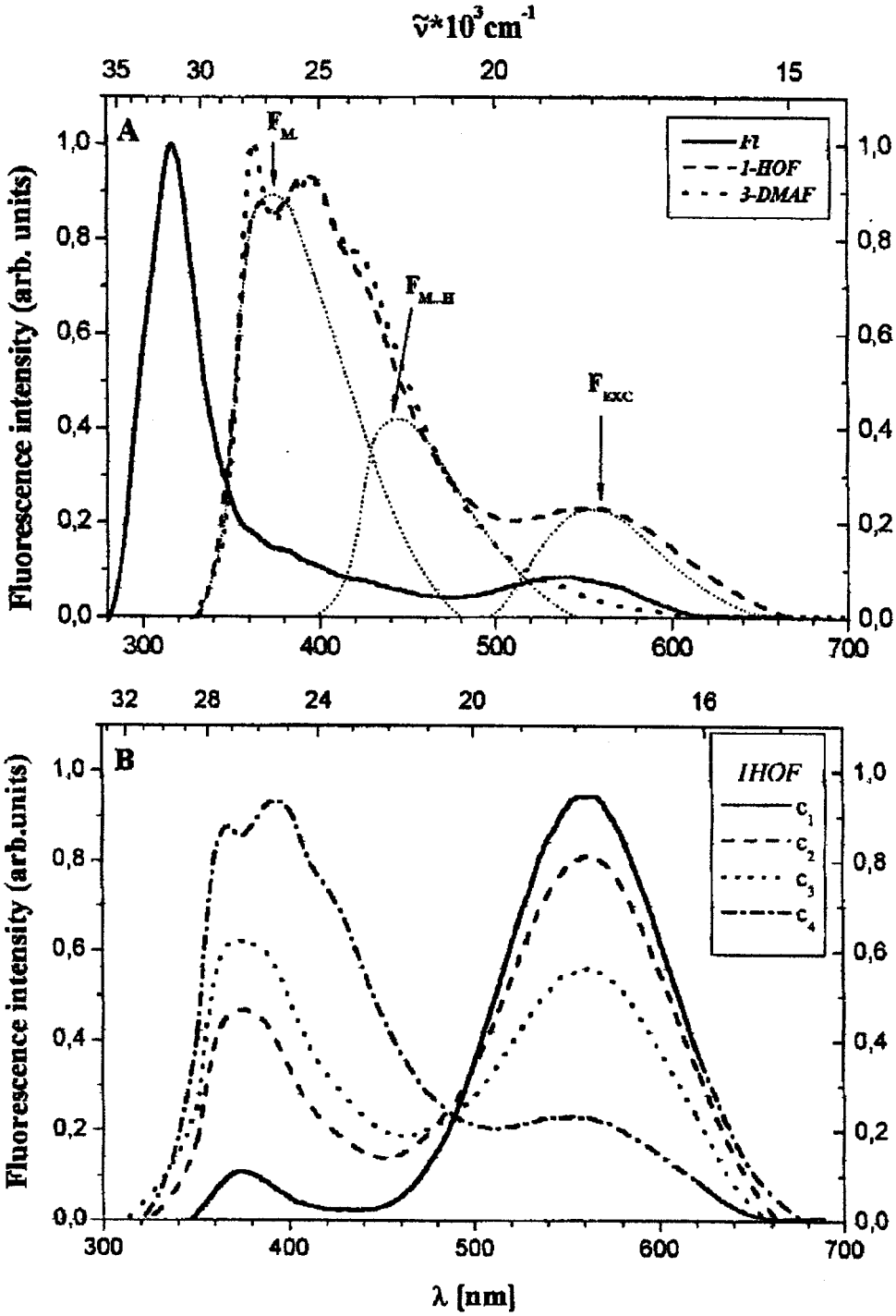

Fig. 2. Fluorescence spectra (A) of FL, 1HOF, and 3DMAF in MeOH ($c = 10^{-3}$ M) and (B) of 1HOF in MeOH for various concentrations, $c_1 = 10^{-3}$M, ... , $c_4 = 5 \cdot 10^{-5}$ M.

of formation of the molecular H-bond solvates respectively. For the H-bond carbonyl group E_r, is of the order 12–18 kJ M^{-1} [11]. Using the determined data of $\tilde{\nu}_M$ and $\tilde{\nu}_{M...H}$ we found that $-\Delta H^* + E_r$ values are about 45 kJ/M. The exact values of the left side of Eq. (1) for the three molecules are collected in Table II. They are greater than the thermal energy (RT ≅ 3 kJ/M). This facilitates additionally the formation of the H-bond complexes.

The excimer fluorescence band at $\lambda_{EXC} \cong 550$ nm is distinctly marked for FL and 1HOF molecules only. For

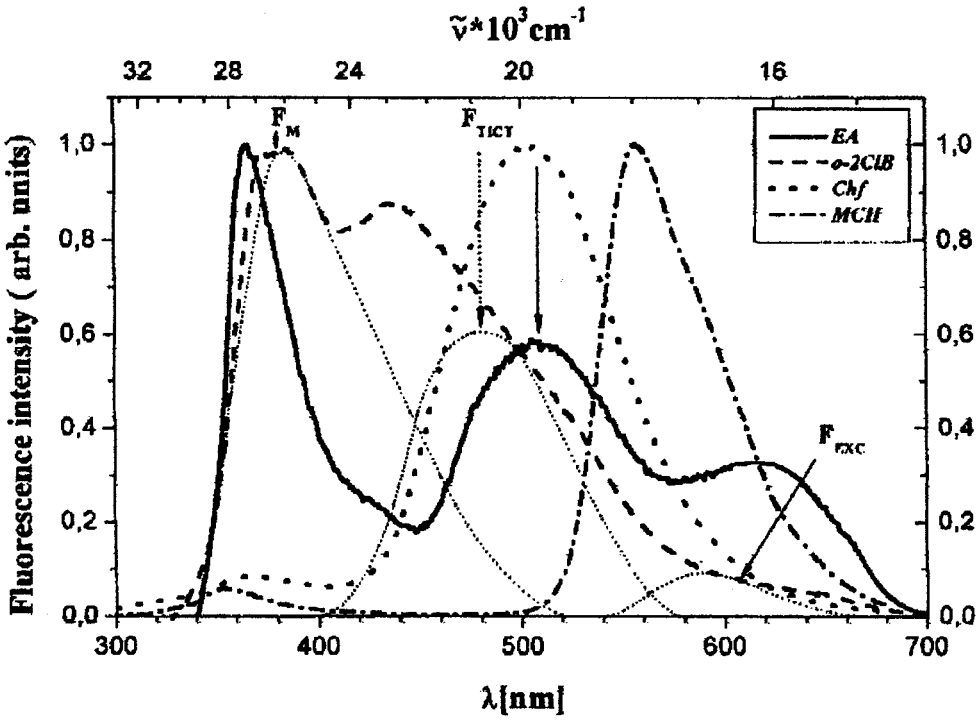

Fig. 3. Fluorescence spectra of 3DMAF in various polar solvents. The arrow indicates the λ_{max} value of the observed fluorescence bands.

3DMAF it is revealed in the long wing of the fluorescence band (see Fig. 2A). We suppose that the excimers of the 1HOP and 3DMAF molecules arise in triplet-triplet annihilation process similar as observed in fluorenone [2]. This process consists of a transfer of energy form one triplet to another to form an excited dimer species according to the sequence [22,23]

$$^1M \xrightarrow{h\tilde{\nu}_A} {}^1M^* \begin{cases} \xrightarrow{k_{ISC}} {}^3M^* \xrightarrow{{}^3M^*} {}^1(M^*{:}M) \xrightarrow{h\tilde{\nu}_{EXC}} 2\,{}^1M \\ \xrightarrow{k_F} M + h\tilde{\nu}_M \end{cases} \quad (2)$$

where ^{1}M, ^{1}M* and ^{3}M* stand for the molecules in the singlet ground, excited and triplet excited states, respec-

Table II. Value of the Heat Formation of H-Bond Complexes, Charge Transfer Isomers, and Excimers in Various Solvents[a]

Compound	Heat of formation (kJMol^{-1}) Assoc. MeOH	Excimer MCH o-2ClB	CT-isomer o-2ClB EA	Onsager cavity radius a_0 (10^{-8} cm)	Dipole moments (D) μ_g	μ_M	μ_{TICT}	μ_{EXC}
Fluorenone (FL)		126.7		1.80[b]	2.96[b]	~2.96		5.57[c]
	47.7	81.9			3.66 ± 0.3[d]	3.08 ± 0.2[d]		
1-Hydroxyfluorenone (1HOF)		78.2		1.94[b]	3.35[b]	~3.55		6.66[c]
	39.8	87.8						
3-Dimethylaminofluorenone (3DMAF)	36.6	123.7	66.6	2.17[b]	5.04[b]	7.20	8.80	7.90[c]
		118.7	90.8					

[a] The dipole moments of the first singlet excited state of FL, 1HOF, and 3DMAF and its emitting species: monomers, μ_M; charge transfer isomer, μ_{TICT}; excimers, μ_{EXC}.
[b] Data calculated using the AM1 method.
[c] In the calculation the Onsager radius of the excimer is assumed to equal $2a_0$.
[d] W. Liptay, H. Weisenberger, F. Tieman, W. Eberlein, and G. Konopka (1968) *Z. Naturforsch.* **23a**, 377–393.

tively. According to the relation (2) the monomer and the excimer emission is observed by steady-state fluorescence measurements. For the excimer formation the conditions are even more favourable since hc ($\tilde{\nu}_M - \tilde{\nu}_{EXC}$) value equals to about 95 kJ/M for FL. In Table II are collected the values of the heat of formation for the excimers of 1HOF and 3DMAF molecules as well.

Figure 3 shows the total emission spectra of the 3DMAF molecule in three polar solvents. Here the spectrum in MCH is given for comparison only. The spectrum in EA consists of three bands: the normal monomer fluorescence band at $\lambda_M = 375$ nm, the excimer fluorescence band at $\lambda_{EXC} = 610$ nm and a new fluorescence band around 510 nm. This band appears in polar solvents only. This new band is attributed to the emission from a twisted intramolecular charge transfer state, S_1(TICT), of an isomer in which the -$N(CH_3)_2$ chromophor donates charge to the skeleton of fluorenone. This phenomenon appears in all polar solvents used. The TICT as well as the excimer fluorescence bands show a large solvent dependent Stokes shift.

Figure 4 show graphically the dependence the Stokes shift of the $\tilde{\nu}_{EXC}$ and $\tilde{\nu}_{TICT}$ value versus the Lippert function f(ε, n). A linear dependence of $\tilde{\nu}_{EXC}$ and $\tilde{\nu}_{TICT}$ *versus* the Lippert function is fulfilled for all molecules under study. It shows that the initial electronic excited states S_1(M) and S_1(TICT) for 3DMAF only have substantial charge-transfer character, whereas the excimers of all three molecules are dipolar character. It is an analogy to the related initial states of the respective transitions in 7-azoindole [15], aminosalicylate, benzanilide [16], anthraquinone derivatives [17,18] and fluorescent exciplexes of aromatic hydrocarbons [25]. As it follows from the paper of Bachshyjew [19], Gryczynski and Kawski [20], Mataga and Kubota [21] and Liptay [22], within a dielectric continuum approximation of the solvent the change of the steady-state Stokes shift is related to the change in the dipole moment, $\Delta\mu = \mu_{ex} - \mu_g$ according to the relation [21,22]

$$\tilde{\nu}_A - E_F = \frac{2(\mu_{ex} - \mu_g)^2}{cha_0^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right) = \frac{2\Delta\mu^2}{cha_0^3} f(n,\varepsilon) \quad (3)$$

In Eq. (3), $\tilde{\nu}_A$ and $E_F = \tilde{\nu}_F(M)$; $\tilde{\nu}_F(TICT)$ or $\tilde{\nu}_F(EXC)$ are the maximum wave numbers of the absorption and fluorescence bands respectively; i.e., fluorescences emitted from the monomer (M), the charge transfer (TICT) isomer or excimer (EXC) excited states. ε and n are the dielectric constant and index of refraction of the solvent, a_0 is the Onsager cavity radius of the solute molecule. The steady-state Stokes shift for the emission bands of FL, 1HOF and 3DMAF molecules plotted against f(ε,n)

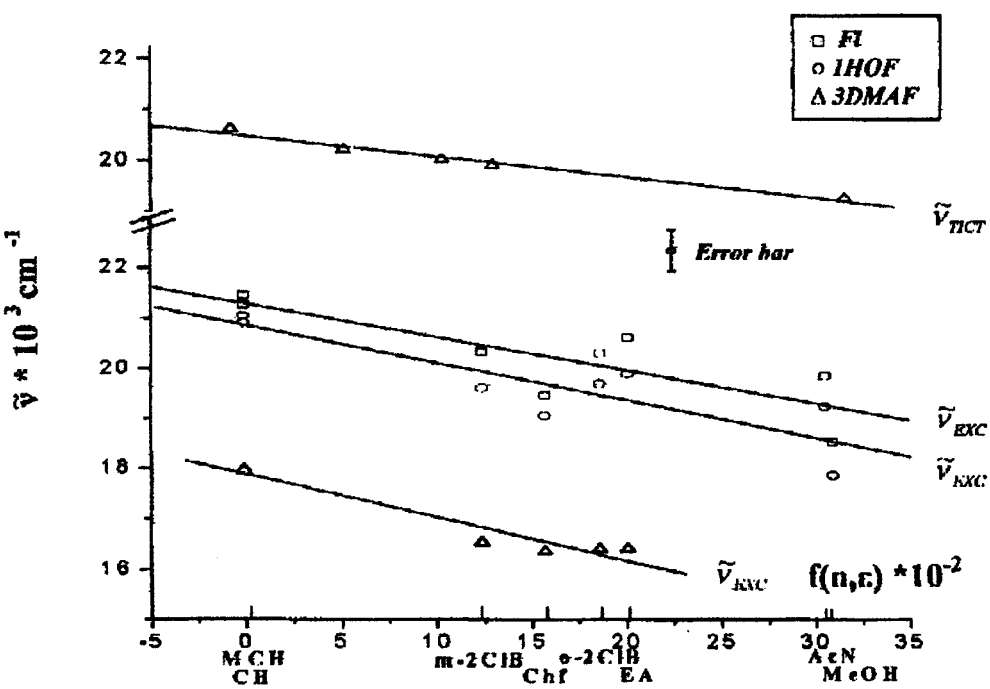

Fig. 4. The maximum wave number of the excimer, $\tilde{\nu}_{EXC}$, and TICT fluorescence, $\tilde{\nu}_{TICT}$, bands *versus* the Lippert f(n, ε) function of FL, 1HOF, and 3DMAF solutions.

can be best approximated by a linear function. Scattering of the data points of the various graphs is quite small (in the error bars) for the solvents used. The correlation coefficients of the linear least-square fit procedure varies between 0.80 and 0.98. It must be noticed that the slope value corresponding to the $\Delta\tilde{\nu}_M = \tilde{\nu}_A - \tilde{\nu}_F(M)$ lines for FL and 1HOF molecules (is equal to zero). It means that the dipole moments of these molecules in the S_1 state do not change, they equal to that of the S_0 state. A difference of the $\Delta\mu = \mu_{ex} - \mu_g$ value is noticed for the S_1 state of 3DMAF. Figure 4 shows graphically the data for the Lippert-Mataga analyses of the TICT isomer and excimer fluorescence of the studied molecules. Since for this species the absorptione spectra are not observed (e.g. in Eq. (3) $\tilde{\nu}_A = 0$ and $\mu_g = 0$) the maximum values of $\tilde{\nu}$ of the respective fluorescence are evaluated according to [25,26].

Table II assembles the dipole moments in the ground μ_g and excited states: μ_M, μ_{TICT} and μ_{EXC}, respectively. The dipole moments of the molecules in the ground state and the Onsager radius a_0 were determine using AM1 calculations by means of the HyperChem program. Analysing the dipole moment data collected in Table II it follows that

- the electron-donating functional groups increase the permanent ground-state dipole moment in comparison to the parent molecule,
- the dipole moment of the S_1 state of 3DMAF monomer molecule is about 40% bigger than that of the S_0 state. It points that the S_1 state has a substantial charge-transfer character,
- the dipole moment of the S_1(TICT) state of the 3DMAF is about 70% larger from that which possesses this molecule in the S_0 state being in thermal equilibrium with the environment,
- the excimers of the studied molecules show dipolar nature similar to that of aromatic hydrocarbons [25]. Its μ values are bigger from that of the monomer in the S_0 and S_1 states.

The μ_{EXC} value given in the last column of Table II can be treated as approximate data only. Thus, we assumed in the calculations that a_0 describes the separation of the excimer components. Also, the molecules are estimated to be spherical. This are crude approximations for the molecules under study. Considering the relatively large uncertainly in the determination of the maximum wave number of the decomposed fluorescence bands and the approximation mode calculating the a_0 values the error $\Delta\mu \cong \pm$ 1D.

The above notice changes of μ appear for many molecules where in the excited state a photoinduced tautomerization, H-bond solvation, aggregation or photoinduced charge transfer phenomenum appears [7,8,10,14, 24,25].

CONCLUSION

The results of the measurements allow to conclude that: the shape of the absorption spectrum of fluorenone and its two derivatives does not depend on the solvents. The shift of the absorption peaks caused by the solvents is small. Some solvents cause notable blurring of the vibration structure in the longwave absorption band. The fluorescence spectrum of fluorenone and its two derivatives is solvent sensitive. Its shape and number of bands depend on the kind of solvent, concentration of solute molecules and on the excitation wavelength.

We suppose that the photoinduced excited-state double proton transfer reaction plays an important role in forming H-bond complexes, tautomeric species and excited dimers specially in alcohol solutions of 1HOF. The three molecules studied in MeOH posses emission spectra in which the normal fluorescence band, F_M, the excimer fluorescence band, F_{EXC}, and the H-bond solvate fluorescence band, $F_{M...H}$, can be distinguished.

The above fluorescence modes were confirmed by the dielectric solvents effects on spectra position and solute concentration studies. For the 3DMAF molecule in polar aprotic solvents an additional fluorescence band appears at $\lambda_{TICT} \cong 500$ nm. It is attributed to the emission of a charge transfer isomer being a result of the donor moiety $-N(CH_3)_2$ twist in respect to acceptor fluorenone skeleton. It is shown that the molecules studied are able to form different kind of emiting species depending on the environment. This process is facilitated by the high surplus of the heat formation energy in comparison with the sum of thermal and activation energy.

By mean of the method of solvent induced shifts of the electronic absorption and emission bands the dipole moment of the excited state of the monomer and TICT isomer have been determined for the molecules under study. It has been shown that the noticed excimers show dipolar nature in all solvents.

The time resolved spectroscopic studies in progress will deliver more detailed information concerning the emission modes in the molecules under study.

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