NATURE OF THE FLUORESCENT STATES OF QUINOLINE ANALOGS OF STYRYL AND DISTYRYLANTHRACENE

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Study of the photophysical properties of quinoline analogs of 9-styryl and 9,10-distyrylanthracenes showed that, in contrast to the case of 9-[β-(2-quinolyl)vinyl]anthracene, the intramolecular geometrical relaxation process plays a decisive role in the formation of the excited state of 9,10-di-[β-(2-quinolyl)vinyl]-anthracene.

As is known, intramolecular geometrical relaxation exerts a marked influence on the photophysical properties of molecules [1-4]. The geometry of the ground and the first excited electronic states may differ considerably, which may be the reason for anomalously large Stokes shifts (up to 11,000 cm^{-1}). This is explainable [1-6] by the increase in the coplanarity of the molecules during excitation. The change in the geometrical symmetry can be recorde by studying the dependence of the fluorescent properties of the molecules on the nature of the environment, the viscosity of the medium and the temperature.

To clarify the nature of the first electronic excited state that is responsible for the fluorescence, we studied the influence of the medium and temperature on the spectral-luminescent properties of 9-[β-(2-quinolyl)vinyl]anthracene (I) and 9,10-di-[β-(2-quinolyl)vinyl]anthracene (II), having a large Stokes shift [7]. Comparison of the monosubstituted and disubstituted compounds I and II was necessary for clarifying the influence of the structural factors on the course of the geometrical relaxation processes of the molecules during excitation.

Figures 1 and 2 show the absorption and fluorescence spectra of the compounds studied in different media, and Table 1 gives their spectral-luminescent characteristics in solvents of different polarity. Table 1 shows that in all solvents, the two compounds have fairly large Stokes shifts (5000-6000 cm^{-1} for the monosubstituted I and 7000-9000 cm^{-1} for the disubstituted II). The fluorescence parameters of the two compounds are independent of the concentration, which indicates an intramolecular mechanism for the formation of the fluorescent states.

The absorption spectra are not very dependent on the nature of the solvent and the temperature. Therefore, the value of the Stokes shift $\Delta\nu_S$ is mainly influenced by the position of the fluorescence spectrum. A decrease in the temperature from 300 to 77°K practically does not affect the position of the fluorescence spectrum of compound I in toluene. The fluorescence maximum of compound I introduced into a polymeric matrix (a polystyrene film obtained from a toluene solution of the polymer) coincides with the maximum of the spectrum in slightly polar solvents (heptane, cyclohexane). The data obtained show that the viscosity has little influence on the value of the Stokes shift. This is also confirmed by the fact that in solvents of high viscosity (ethylene glycol, butylene glycol), $\Delta\nu_S$ is large and coincides with the Stokes shift in solvents with much lower viscosity but with similar polarity. Thus $\Delta\nu_S$ is approximately the same in ethylene glycol and in acetonitrile, whose dielectric constants are similar (37.7 and 37.5), while the viscosities strongly differ (20 and 0.35 cP). These facts indicate that for the monosubstituted anthracene I, the formation of the fluorescent state is not accompanied by a considerable change in the mutual disposition of the large chromophore groups, which should be strongly influenced by the viscosity of the medium. Nevertheless, the fairly large Stokes shift indicates that the nuclear configuration and the electronic density are changed, while the general form of the potential surface of the excited state is retained. A change in the dipole moment during the excitation may also take place.

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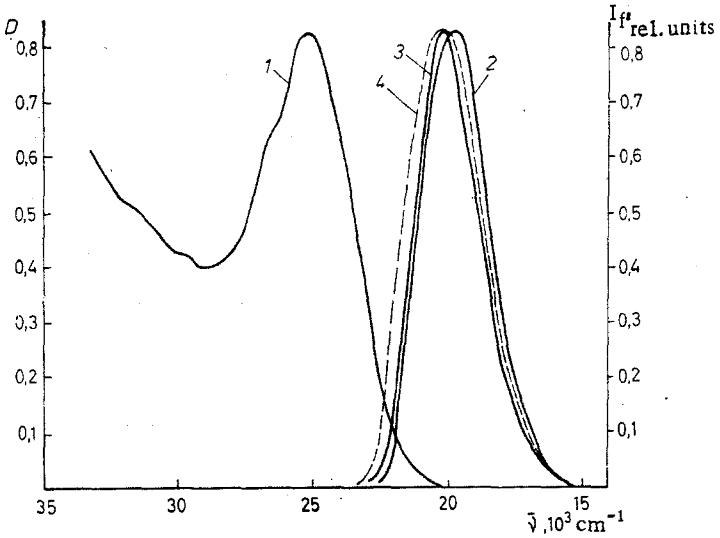


Fig. 1. Absorption (1) and fluorescence (2-4) spectra of compound I: 1, 2) in toluene at 300°K; 3) in toluene at 77°K; 4) in polystyrene film.

As the result of a great change in the nuclear configuration during the excitation, by which the structure becomes more planar (which is accompanied by a relative shift of the potential surfaces of the ground and excited states), the mirror symmetry of the absorption and fluorescence spectra should be disturbed. Moreover, the values of φ_f/τ_f and the radiative rate constant k'_f, obtained from the absorption spectra [1] may also change. For compound I, an ideal mirror symmetry of the spectra is retained in all solvents (adherence to the mirror symmetry rule was verified according to [8]), while the values of $\varphi_j/\tau_f = k_f$ and k'_f (calculated according to the Bowen and Wax formula [9]) coincide within experimental error (Table 2). This serves as an additional confirmation for the absence of appreciable geometrical changes in the molecular structure during the excitation of a monosubstituted anthracene I.

The polarity of the solvent influences the value of $\Delta\nu_S$, which agrees with certain redistribution of the electron density. The change in the dipole moment of the molecule of I during excitation was evaluated from the dependence of the value of $\Delta\nu_S$ on the polarity parameter $f(\varepsilon, n)$ [10], and was found to be equal to approximately 10 D.

$$f(\varepsilon, n) = (\varepsilon-1)/(2\varepsilon+1) - (n^2-1)/(2n^2+1),$$

where ε is the dielectric constant; n, the refractive index of the solvent.

In disubstituted anthracene II, the position of the fluorescence spectrum is strongly dependent on the viscosity of the solvent. Increase in the viscosity (transition from toluene to

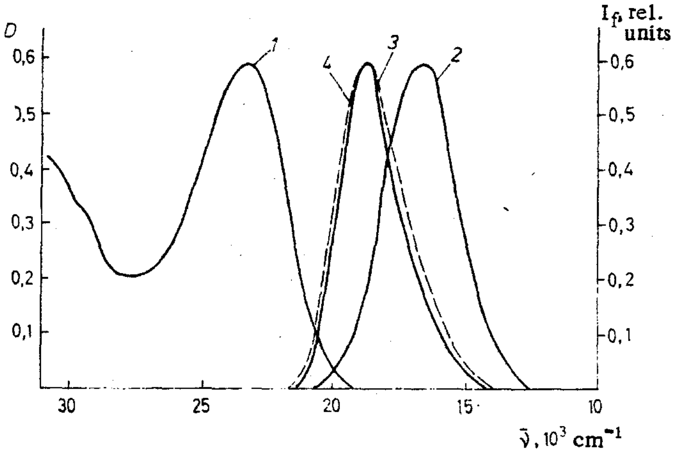


Fig. 2. Absorption (1) and fluorescence (2-4) spectra of compound II: 1, 2) in toluene at 300°K; 3) in toluene at 77°K; 4) in polystyrene film.

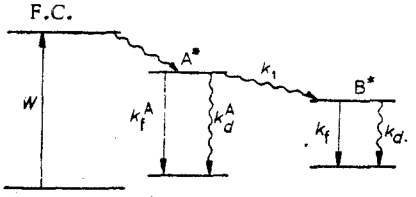
TABLE 1. Spectral-Luminescent Characteristics of Compounds I and II in Different Solvents

Solvent	Compound I		Compound II	
	ν_{max}^{abs}, cm^{-1}	ν_{max}^{fl}, cm^{-1}	ν_{max}^{abs}, cm^{-1}	ν_{max}^{fl}, cm^{-1}
Heptane	25 510	20 200	23 810	16 670
Toluene	25 510	19 800	23 470	16 950
Ethyl acetate	25 380	19 680	23 580	15 150
Butyl acetate	25 380	19 680		
Chloroform	25 380	19 080	23 260	15 150
CCl_4	25 130	19 610		
Cyclohexane	25 440	20 000		
Methanol			23 580	15 380
Ethanol	25 380	19 050		
n-Propanol			23 470	15 150
Acetone	25 380	19 230	23 530	14 710
Acetonitrile	25 640	19 230	23 530	14 490
Ethylene glycol	25 250	18 690		
Butylene glycol	25 300	19 000	23 540	18 200

ethylene glycol or butylene glycol) leads to a short-wave shift of the fluorescence spectrum. On cooling the toluene solution of compound II to 77°K, when the viscosity sharply increases, the spectrum is shifted to the short-wave region still more strongly (Fig. 2) and coincides with the spectrum of this compound in a polystyrene film. This indicates a more considerable change than in the case of monosubstituted I in the mutual disposition of the large chromophore groups, and increase in the effective length of the conjugation chain during the formation of a fluorescent state of compound II. In rigid matrices (glass, polymeric film), this process should be strongly hindered. Since in a glasslike matrix at 77°K the fluorescence spectrum completely coincides with the spectrum in polystyrene at 300°K, while the latter is independent of the temperature, it can be stated that the viscosity plays the decisive role.

The polarity of the solvent also influences the value of $\Delta\nu_s$ for compound II. Evaluation according to [10] of the change in the dipole moment during the excitation gave the value of 12 D. It can thus be stated that in the case of a disubstituted anthracene II, the value of the Stokes shift is determined by two processes. The first is analogous to that described for the monosubstituted I and determines the value of the Stokes shift in rigid media. The other is related to the increase in the coplanarity of the molecule during excitation, leading to increase in the π-conjugation system in the molecule. In contrast to the former case, the second process should lead to a disturbance of the mirror symmetry of the absorption and fluorescence spectra, which in fact is experimentally observed.

The processes of the formation of the fluorescent state of compound II can be described by the following scheme:



After excitation of the molecule to a Franck–Condon state (F.C.), a rapid relaxation takes place into the state A*, similar to the fluorescent state of compound I. No fluorescence is observed from this state at 300°K in solvents with low viscosity, since a rapid ($k_1 \ll k_f^A$) change in the nuclear configuration takes place, which is accompanied by rotation of the different chromophores and compression of the structure of the molecule with the formation of state B*, whose fluorescence we in fact observe.

We studied the dependence of the quantum yields φ_f and attenuation time τ_f of the fluorescence of compound II on temperature in the range of 290-350°K in toluene and heptane. We found that the value of φ_f decreases with increase in the temperature, while τ_f remains unchanged. According to the above scheme, the fluorescence quantum yield from state B* is

$$\varphi_f=\frac{k_1}{k_1+k_f^A+k_d^A}\tau_f k_f\approx\frac{k_1}{k_1+k_d^A}\tau_f k_f, \qquad (1)$$

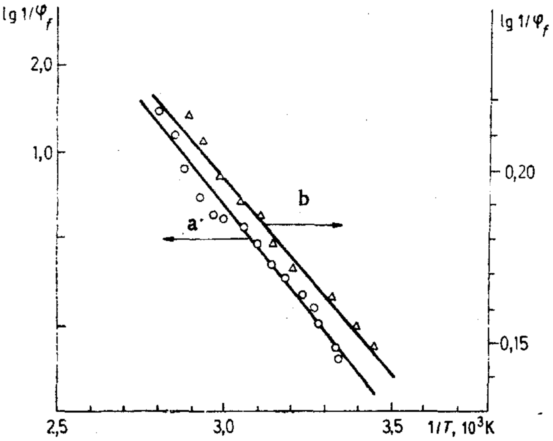


Fig. 3. Dependence of reciprocal fluorescence quantum yield on reciprocal temperature for compound II in heptane (a) and toluene (b).

TABLE 2. Photophysical Characteristics of Compounds I and II in Different Solvents at 300°K

Compound	Solvent	φ_f	τ_f, nm	φ_f/τ_f, 10^8 sec^{-1}	k'_f, 10^8 sec^{-1}
I	Heptane	0,45	3,1	1,3	
	Toluene	0,35	2,5	1,4	
	Cyclohexane	0,5	3,5	1,4	1,2
II	Heptane	0,5	4	1,2	
	Toluene	0,65	4	1,6	1,9

where k_1 is the rate constant of the formation of state B* from A*, while $K_f{}^A$ and $k_d{}^A$ are the rate constants of fluorescence and nonradiative deactivation from state A*. If we assume that constants k_1 and $k_d{}^A$ depend on temperature

$$k_1 = k_1{}^0 \exp(-E_1/RT), \quad k_d{}^A = k_d{}^{A0} \exp(E_d{}^A/RT),$$

then from (1) we obtain

$$1/\varphi_f = 1/k_f\tau_f + \frac{k_d{}^{A0}}{k_1{}^0 k_f\tau_f} \exp\frac{E_1 - E_d{}^A}{RT}. \tag{2}$$

Moreover, from Eq. (1) it follows that

$$\varphi_f = \frac{k_f}{1 + \frac{k_d{}^{A0}}{k_1{}^0} \exp\frac{E_1 - E_d{}^A}{RT}} \tau_f = \alpha\tau_f, \tag{3}$$

wherein the expression before the term τ_f in the left-hand side of the above equation has been designated as α.

By measuring the value of φ_f/τ_f experimentally, we obtain α instead of k_f, which should be dependent on the temperature. Hence it follows that the coincidence of the values of φ_f/τ_f and k'_f obtained for the disubstituted compound II (Table 2) is only apparent.

Using Eq. (2), we can calculate the difference in activation energies $E_1 - E_d{}^A$. The dependence of log $(1/\varphi_f)$ on 1/T in toluene and heptane are linear (Fig. 3). It can be assumed that the first term in (2) is small, and from the slope of the corresponding lines we obtain values of $E_1 - E_d{}^A$ equal to 8.5 and 0.4 kJ/mole in heptane and toluene, respectively.

The data obtained show that the intramolecular geometrical relaxation process plays a decisive role in the formation of the excited state of disubstituted anthracene II.

EXPERIMENTAL

The synthesis and spectral-luminescent properties of compounds I and II were described by us previously in [7].

The electronic absorption spectra were measured on a Unicam SP-8000 spectrophotometer. The fluorescence spectra were measured on a Jobin–Yvon spectrofluorimeter. The fluorescence spectra were corrected for the spectral sensitivity of the apparatus. The absolute fluorescence quantum yields were determined by a relative method. Quinine bisulfate in 0.1 N sulfuric acid ($\varphi_f = 0.55$ [11]) and 3-aminophthalimide in ethanol ($\varphi_f = 0.6$ [12]) were used as standards.

The fluorescence attenuation time was measured on a pulse nanosecond fluorimeter in a single proton counting regime [13]. The duration of the exciting flash was 1-1.5 nsec. The real attenuation time was determined from the formula $\tau_f = (\tau_{exp}^2 - \tau_{flash}^2)^{1/2}$ [14]. The accuracy of the determination was 10-15%.

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3-ARYL-2-BENZYL -1,2-DIHYDROQUINOXALINES

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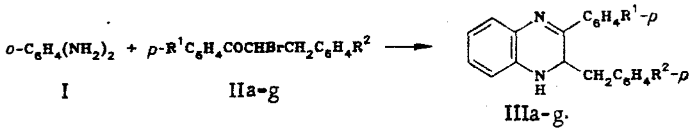
The reaction of 1,2-phenylenediamine with 2-bromo-1,3-diaryl-1-propanones led to stable and crystalline 3-(4-R-phenyl)-2-(4-R'-benzyl)-1,2-dihydroquinoxalines.

Aromatic derivatives of 1,2-dihydroquinoxaline are inherently powerful fluorescing agents with major Stokes shifts [1], but they are chemically unstable. Their tendency to aromatize decreases their practical utility. In our search for increasing the stability of 1,2-dihydroquinoxalines we have synthesized 3-(4-R-aryl)-2-(4-R'-benzyl)-1,2-dihydroquinoxalines (IIIa-g) by treating 1,2-phenylenediamine (I) with 2-bromo-1,3-diaryl-1-propanones (IIa-g) in methanol in the presence of sodium acetate:



II, III a, g $R^1=H$, b $R^1=CH_3$, c $R^1=OCH_3$, d $R^1=C_6H_5$, e $R^1=Cl$, f $R^1=Br$;
a-e $R^2=H$, g $R^2=Cl$

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