

INTRAMOLECULAR ENERGY TRANSFER IN LASER ACTIVE BICHROMOPHORIC MOLECULES

by

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(Received December 1, 1981)

The results obtained by the examination of the fluorescence of two laser active bichromophoric dyes are described. The pure electron transition frequencies belonging to the $S_0 \rightarrow S_1$ transition and the natural decay times of the dyes were calculated and the decay times were also measured. The fundamental polarisation spectra of the examined materials were recorded and the angles between the emission oscillator and the absorption oscillators of the dyes were determined.

1. The luminescence characteristics of bichromophoric molecules differ from those of the usual luminescent materials. Generally the characteristic absorption bands of the two chromophores can be distinguished clearly from each other in their absorption spectra and, in certain cases, the emission of both chromophores can be observed [1]. This can be explained with the fact that between two different chromophores of the bichromophoric molecule, coupled with longer or shorter saturated link, energy transfer takes place during the life time of the excited state. In the energy transfer process the one chromophore has the role of a donor, the other chromophore that of an acceptor. The principal condition of the energy transfer is the same as it is for separated molecules [2], the emission spectrum of the donor-moiety and the absorption spectrum of the acceptor-moiety must overlap each other strongly, in this case the interaction energy among the molecule-parts may be sufficiently high to produce the transfer process. So far the number of the bichromophoric compounds, which were examined in detail in order to clear up of the energy transfer mechanism, are about fifty. However, in most cases no unanimous stand could be taken the character of the transfer. The main reason of this is the fact that the spatial orientation of the distance of the donor- and acceptor-parts compared to one another in the molecules, is not known, or it is not fixed. During the first relevant examination the chromophor moieties were joined by $-(CH_2)_n-$ links, by increasing the link-parts, no change was experienced in the efficiency of the energy transfer [3].

Later, the chromophores were joined *e.g.* to a rigid steroid bridge or to the end of a rod-like molecule-part to fasten the distance of the donor-acceptor [4], then role of the orientation of the chromophore-parts was examined, too [5]. Transfer was observed, in certain cases, between the singlet levels of the donor and the acceptor; in other cases, among the triplet states: sometimes in both at the same time. According to previous observations, energy transfer may take place essentially with any orientation and the transfer between triplet states has a smaller radius of action than that of the singlet ones.

In this paper we report on our results obtained by the examination, of two laser active bichromophoric dyes on fluorescence properties. The bichromophoric mate-

rials studied by us were produced by Prof. W. LÜTTKE and B. LIPHARDT [6] in order to obtain fluorescent dye laser solutions of good efficiency [7].

2. When two dye molecules are at a short distance R from each other in the solution (and R is much shorter than the mean wavelength of the luminescence of the donor molecule) then in FÖRSTER's view [2] the occurrence k_T of the resonance energy transfer is proportional to $1/R^6$, and k_T^{-1} will be equal to the natural decay time of the luminescence of the donor, if

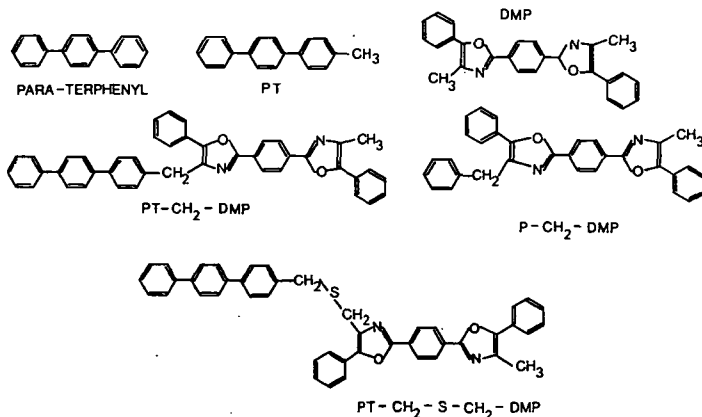
$$R_0^6 = \frac{9(\ln 10)\kappa^2\Phi^D}{128\pi^5 N n^4} \int_0^\infty \varepsilon^A(\lambda) f_q^D(\lambda) \lambda^4 d\lambda. \quad (1)$$

The quantities occurring in it are: $\varepsilon^A(\lambda)$ is the molar decadic extinction coefficient of the acceptor, $f_q^D(\lambda)$ means the normalised fluorescence quantum spectrum of the donor, Φ^D the absolute quantum yield of the donor, n the refractive index of the solution, and N Avogadro's number. Factor κ^2 occurring in Eq. (1) is a simple function of the angles between the emission oscillator of the donor, the absorption oscillator of the acceptor, as well as the straight line joining these two oscillators and the molecules.

In order that Eq. (1) be valid the distance between the molecules needs be much greater than the dimensions of the molecules. Therefore if the donor and the acceptor are combined to bichromophoric molecules, Förster's equation gradually loses its validity and the mechanism of energy transfer can be interpreted in a more complicated fashion [2].

Below the notions of Förster's theory shall also be used for the little value of R , although this procedure proves occasionally to be formal. As a matter of fact the importance of other interaction is proved to be greater than that of Förster's mechanism for molecule distances shorter than 1.2-1.5 nm.

3. The examined dyes have been made available for us by the Laser Physical Group of Max Planck Institute in Göttingen. The components of the bichromophoric compounds are the paraterphenyl and the 4-methyl-paraterphenyl (PT), the *p*-phenylene-bis-(5-phenyl-4-methyl-2-oxazole), dimethyl-POPOP (DMP) for short. The chromophores PT and DMP in the bichromophores were joined by groups-CH₂- and -CH₂-S-CH₂-respectively. Their designation below will be PT-CH₂-DMP and PT-CH₂-S-CH₂-DMP respectively. Besides we investigated the *p*-phenylene-bis [5-phenyl-4-methyl(4'-benzyl)-2-oxazole] (P-CH₂-DMP) which may regarded as an acceptor-model. The structural formulas of the compounds are the following:



We used dioxane, cyclohexane, glycerol and methanol (puriss., REANAL) as solvents. The purifying of the dioxane and the glycerol was made after dehydration by distillation, the purifying of cyclohexane took place on a Kieselgel column. The impurities that might be left over in the solutions used showed no considerable absorption at wavelengths longer than 250—260 nm.

We recorded the absorption spectra with a spectrofluorimeter of OPTON PMQ 3 type, the fluorescence and polarization spectra with a fluorescence spectrometer of PERKIN ELMER MPF 44 A type. The yield of the dye solutions was determined by using a relative method, with the above mentioned instruments, by means of solution of quinine sulphate solved in 1 n H_2SO_4 , practically in the manner described in [8]. The quinine sulphate was a SIGMA production, its yield, according to earlier measurements [9], agreed well with the value of 0.546, accepted by the literature [10]. For the measurement of the viscosity HÖPPLER's viscosimeter was used.

For the fluorescence and polarization measurements, the concentration of the solutions was between $5 \cdot 10^{-6}$ — $5 \cdot 10^{-7}$ M, the thickness of the square-based prism cells used was 0.3 cm and 1 cm respectively.

The published fluorescence spectra may be regarded as true fluorescence spectra. When evaluating the spectra these were properly corrected, taking into consideration the reabsorption; for different combinations of the layer thickness and concentration used, the secondary fluorescence had no considerable influence on either the spectra, or on the values of the polarization, this fact was verified by calculation [11].

The degree of polarization of the light passing through polaroid filters serving as accessories of the PERKIN ELMER instrument used for polarization measurements, was determined and on the ground of this knowledge, the measured values were corrected [12].

The decay time of the fluorescence of the dye solutions was measured with a phase fluorometer [13]. The concentration of the solutions was 10^{-4} M, the excitation wavelength was 365 nm.

4. The examined absorption and emission spectra of the dyes solved in dioxane are presented in Fig. 1.

According to our preliminary measurements it is preferable to gain the absorption of the bichromophoric compound by using a linear combination of the absorption spectra of the 4-methyl-paraterphenyl and the DMP than that of the absorption spectra of paraterphenyl and the DMP. This fact can be attributed to the influence of the methyl moiety joining on paraterphenyl as a result of which the absorption maximum shifts to the longer wavelengths by 5 nm. Practically, an increase can be observed in this influence when substituting to the hydrogen of the methyl group methyl-POPOP and -S- CH_2 -DMP-moiety, respectively. Thus the absorption of the bichromophoric compounds can not be combined additively, as a result of the absorption of the components, and the difference shows a distinct maximum at approximately 300 nm. It can be observed on Fig.1 that the band of PT is deformed more by the influence of the group containing sulphur than by that of the DMP. The influence of the PT-part on the band of the DMP is small, but that on the PT- CH_2 -DMP results a shift of the spectrum towards the shorter wavelengths in the region of 320—410 nm. The substitution of the phenyl-moiety to the hydrogen of the methyl-moiety results in a similar but, in degree smaller change in the absorption of the DMP (see Fig.1.D).

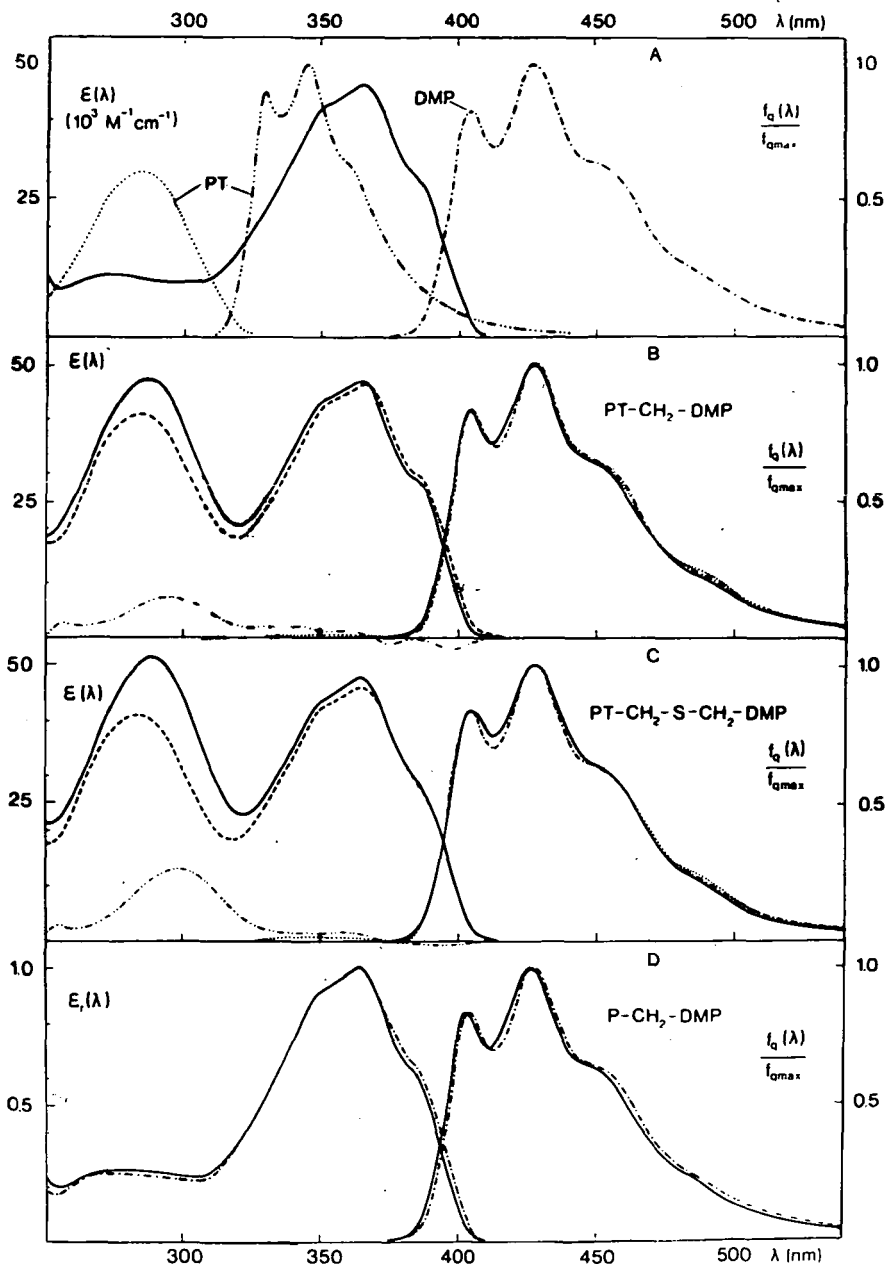


Fig. 1. A: absorption and fluorescence spectra of the methyl-paraterphenyl and ——— respectively, and the corresponding spectra of the dimethyl-POPOP ——— and ——— respectively. The designations in figures B, C and D are: ——— are the absorption and fluorescence spectra of the indicated compounds (the wavelength of the exciting light is: $\lambda_{exc} = 365$ nm); is the fluorescence spectrum of the indicated compounds for an exciting wavelength of 290 nm; ——— are the fluorescence spectra of the DMP ($\lambda_{exc} = 365$ nm). The designations in figures B and C are: ——— is the sum of the absorption spectra of the PT and the DMP; is the difference between the absorption spectrum of the bichromophore and the sum of the absorption of the components. The designation in figure D is: ——— is the absorption spectrum of the DMP

The fluorescence spectrum of the bichromophoric compounds recorded with an exciting light of a wavelength of 365 nm agrees approximately with that of the DMP, but for the PT-CH₂-DMP and the P-CH₂-DMP a distinct though small shift towards the smaller wavelengths appears in the same manner as in the absorption.

The fluorescence spectrum of sulphur containing bichromophore solved in dioxane, apart from the perceptible fading of the vibration structure, coincides with the spectrum of the DMP. However, in cyclohexane, a distinct long wavelength shift may be observed, in spite of the fact that in this solution the absorption spectra of the bichromophore and of the DMP agree almost entirely within the band of the DMP. The depicted deviations of the measured spectra can not be attributed to measuring errors.

The emission spectra of the bichromophoric compounds are independent of the wavelength of the exciting light, while this oscillates in the range of 320—380 nm. For the fluorescence spectra recorded when $\lambda_{exc} = 290$ nm, the fluorescence of the paraterphenyl-moiety may be observed, and a little change can be seen in the band of the DMP, as well. Unfortunately, owing to its very low intensity, we could not record exactly the emission spectrum of the PT-moiety. Its intensity, even at a maximum point, is not more than 0.7 per cent of the maximum intensity of the DMP-moiety in dioxane, and it is 1.5 per cent in cyclohexane for both the bichromophores PT-C-DMP and the PT-CH₂-S-CH₂-DMP (Fig. 2).

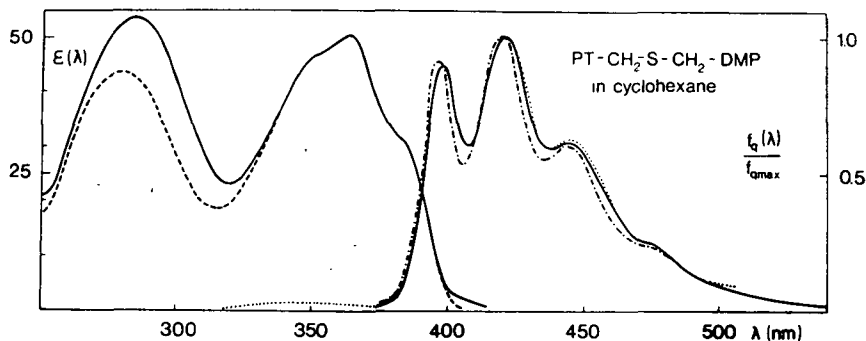


Fig. 2. The absorption and emission spectra of the PT-CH₂-S-CH₂-DMP in cyclohexane solution. The designations are the same as those of the B and C parts in Fig. 1

The small emission of the PT-part can be supposed to result from PT existing as impurity in the bichromophoric compound, but in that case, the conditions of intensity do not change in different solvents, because the yield of the components and that of the bichromophores do not differ considerably in the two solvents.

We mention here that a significant increase in the emission of the PT-part was experienced, when the PT-CH₂-DMP bichromophore was solved in a mixture of dioxane-methanol-glycerol in order to increase the viscosity.

The quantum yield of the fluorescence of the DMP, the PT-CH₂-DMP and the PT-CH₂-S-CH₂-DMP was shown to be constant with a deviation of plus or minus 5 per cent, owing to error in the measurement, in the region of 280—385 nm. The well-known anti-Stokes dropping of the yield function begins where the exciting wavelengths are longer than 385 nm.

The absolute quantum yield of the fluorescence was determined for the PT by using an exciting wavelength of 280 nm, and that of 365 nm for the other compounds. The yields of the DMP and the bichromophores do not differ significantly.

The decay time of all compounds except the PT was determined. The decay time of the DMP and PT-CH₂-DMP are nearly identical, that of the PT-CH₂-S-CH₂-DMP is slightly smaller.

The data concerning the maximum points of the spectra, the maximum values of the molare decadic extinction coefficients, the yields and the decay times are summarized in Table I.

5. The pure electron transition frequencies belonging to S₀→S₁ transition of the dyes were determined by using the measured absorption and emission spectra, in the manner described in [14] by establishing the extreme point of functions $\varphi_i(\nu)$:

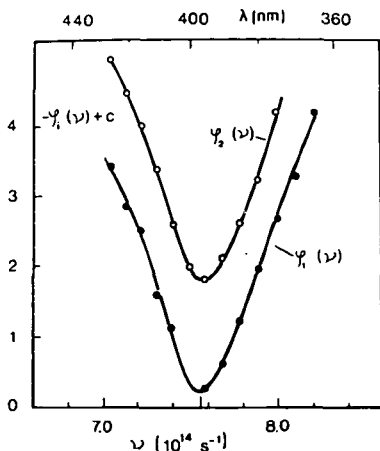
$$\begin{aligned}\varphi_1(\nu) &= \ln [\varepsilon(\nu)\Phi(\nu)\nu^{-1}] - (h\nu/2kT), \\ \varphi_2(\nu) &= \ln [f_q(\nu)\nu^{-3}] + (h\nu/2kT).\end{aligned}\quad (2)$$

In the above equations ν is the frequency, h is Planck's constant, k is Boltzmann's constant, and T the absolute temperature. The extreme value places of the functions $\varphi_1(\nu)$ and $\varphi_2(\nu)$, respectively, showed a good accordance with one another, e.g. the functions $\varphi_i(\nu)$ concerning the PT-CH₂-DMP solution solved in dioxane are presented in Fig. 3. The mean values of pure electron transition frequencies determined such manner are reported in Table I. The value of the so called effective temperature T^* , was also determined in the modified Stepanov's relation [15]

$$f_q(\nu) = D'\Phi(\nu)\varepsilon(\nu)\nu^2 \exp(-h\nu/kT^*) \quad (3)$$

for the examined solutions. Within the equation, D' is a constant independent of frequency. T^* provides a certain information about the energy distribution developing in the excited state. The calculated value of T^* (see Table I) is generally higher than the actual temperature of the solution, and only the data of T^* about the solution in cyclohexane of the PT-CH₂-DMP show that the emission of the DMP-part by excitation of the PT-part takes place through a distribution at a higher temperature than that resulting from the excitation of the DMP-part.

Fig. 3. The functions $\varphi_i(\nu)$ concerning the PT-CH₂-DMP solution in dioxane



The natural decay time τ_0 of the examined material was calculated with the aid of Strickler-Berg's equation given by FÖRSTER [20], the strict prerequisites of its validity being that the mirror image symmetry should be complete:

$$\tau_0^{-1} = 8\pi \cdot 2.303 \cdot 10^3 n^2 c^{-2} N^{-1} \int_0^{\infty} (2\nu_0 - \nu)^3 \nu^{-1} \varepsilon(\nu) d\nu \quad (4)$$

(in Eq. (4) c is the speed of light in a vacuum). Two major problems arise in connection

Table I

Solvent	Material	λ_a (nm)	λ_e (nm)	$\epsilon(\lambda_a)$ $10^3 M^{-1} cm^{-1}$	ν_0 $10^{14} s^{-1}$	$T^*(K)$		τ_0 (ns)	τ_{calc} (ns)	τ (ns)	ϕ	p_0		θ ($\theta_A, \theta_D, \theta_{DA}$)	
						λ_{exc} (nm)						λ_{exc} (nm)		λ_{exc} (nm)	
						290	365					280	365	280	365
di-oxane	para-terphenyl	280	340	31.8	9.40	329	—	1.73	1.56	—	0.90	0.44 ⁽²⁾	—	—	—
	PT	285	345	30.2	9.30	318	—	1.87	—	—	—	0.44 ⁽¹⁾	—	18°	—
	DMP	365	427	46.2	7.552	—	318	1.97	1.62	1.60	0.82	0.0	0.47	55°	13°
	PT-CH ₂ -DMP	365	426	47.0	7.563	303	302	1.93	1.60	1.61	0.83	-0.18	0.48	68° ± 5°	10.3°
	PT-CH ₂ -S-CH ₂ -DMP	365	427	47.5	7.575	324	319	1.87	1.49	1.48	0.80	-0.065	0.48	59° ± 2°	10.3°
	P-CH ₂ -DMP	365	427	—	7.570	—	315	—	—	—	1.50	0.78	—	—	—
cyclo-hexane	para-terphenyl	275	338	31.2	9.532	314	—	1.69	1.37	—	0.81	—	—	—	—
	PT	280	342	31.4	9.42	—	—	1.66	—	—	—	—	—	—	—
	DMP	365	420	50.3	7.642	299	295	1.73	1.38	—	0.80	—	—	—	—
	PT-CH ₂ -DMP	363	420	52.6	7.680	367	342	1.52	1.23	—	0.81	—	—	—	—
	PT-CH ₂ -S-CH ₂ -DMP	365	421	—	7.642	346	346	—	—	—	—	—	—	—	—
	P-CH ₂ -DMP	363	420	45.2	7.686	—	331	1.56	—	—	—	—	—	—	—

λ_a is the maximum point of the long wavelength absorption band

λ_e is the maximum point of the emission spectrum

⁽²⁾ literary data [17], ⁽¹⁾ solvent: mixture of methanol-glycerol

with the applicability of this equation. The one is that the mirror image symmetry rule is obviously not valid for the bichromophoric compounds and for the DMP, the other is that the main absorption band belonging to the $S_0 \rightarrow S_1$ transition cannot be clearly distinguished from the other absorption band. In spite of this, the agreement is surprisingly good between the decay times $\tau_{\text{calc}} = \Phi\tau_0$, calculated from τ_0 , and the measured one: τ_m (see Table I).

6. In order to determine the angle between the emission and absorption oscillators of the bichromophoric compounds and their components, the polarization spectra of the dyes were recorded. In order to determine the fundamental polarization, the PT and the DMP was solved in a mixture of methanol and glycerol, and the viscosity of the solution was changed by increasing of the temperature from 10 to 50 centigrades. The viscosity of the solution in this temperature range alternated between 5 and 0.5 Pa · s. The bichromophoric compounds in suitable concentration are not dissolvable in a mixture of methanol and glycerol. Thus they were solved in dioxane and the viscosity in this case was also decreased in the range of 0.16-0.08 Pa · s by changing the temperature from 12 °C to 48 °C. An essential change in the emission spectrum and the yield was not experienced for this temperature interval. The viscosity of the solutions was determined with measurement at each temperature.

The fundamental polarization value p_0 was determined from the degree of polarization p belonging to different viscosities η and temperatures T with the aid of Perrin-Levshin's relation [16]

$$p^{-1} = p_0^{-1} + \left(p_0^{-1} - \frac{1}{3} \right) \frac{k\tau T}{v\eta} \quad (5)$$

with extrapolation to infinitely great viscosity. (In Eq. (5) v is the molecule volume.) The function $p = f(T\eta^{-1})$ was a straight line for each examined material.

The fundamental polarization spectra are presented in Fig. 4. The absorption spectra of the indicated compounds are also plotted for the sake of clarity in Fig. 4. It should be noted that when recording the spectra the polarized fluorescence of each material was observed at a maximum of the fluorescence spectrum, as the polarized spectra show there a maximum.

The following can established from the polarization spectra:

The degree of polarization in the mean absorption band of the DMP increases slightly with an increase in the wavelength. There is no conspicuous difference between the polarization of the chromophores and that of the DMP at wavelengths longer than 330 nm. On the other hand, the deviation of the polarization spectra in the absorption band of the PT is obvious. While the value of p_0 for the DMP is nearly zero in the range of 280-290 nm, the value of p_0 for the PT-CH₂-S-CH₂-DMP is approximately -0.07 and for the PT-CH₂-DMP it is about -0.18. The values of p_0 for all of the three materials start increasing from 295 nm, but the slopes of the curves are different.

In Fig. 4, the polarization spectrum of the PT is also plotted, reaching a value of 0.44 after an initial decrease, which is good agreement with the literary data [17].

As the degree of fundamental polarization was known to us, the angles θ between the emission and absorption oscillators of molecules were calculated, in terms of the relation [2]

$$\cos^2\theta = (1 + 3p_0)/(3 - p_0). \quad (6)$$

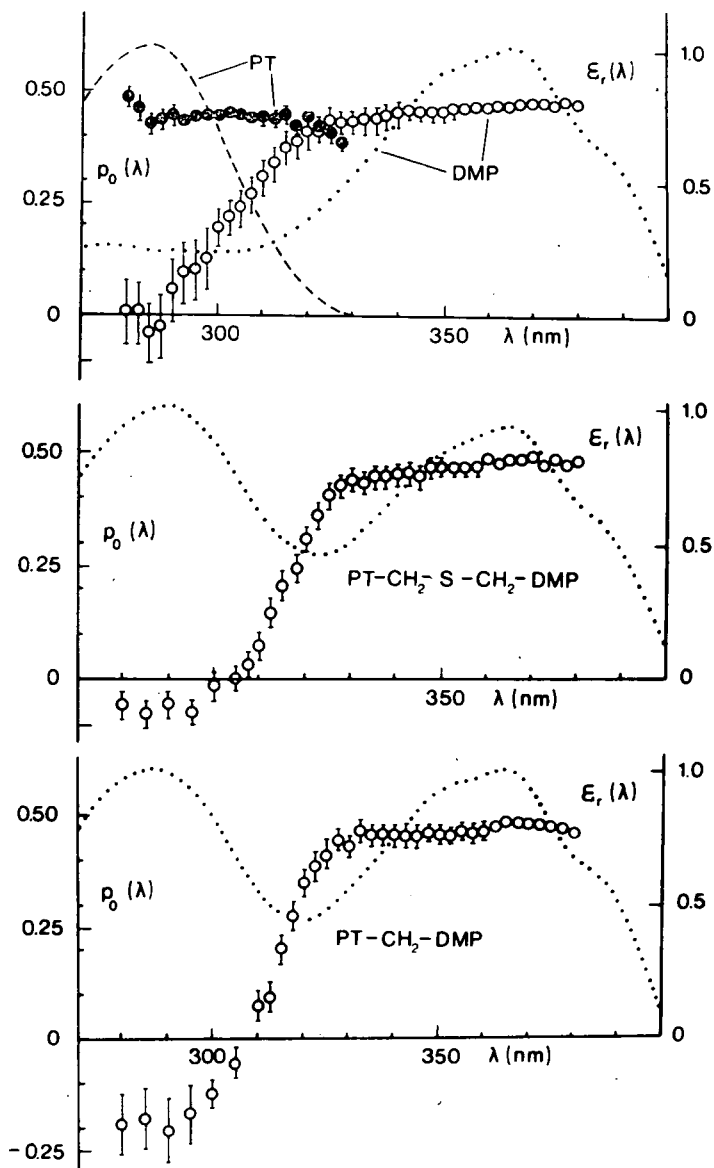


Fig. 4. Polarization spectra marked with ● and ○, respectively, and absorption spectra marked with — — — and ······ respectively, of the bichromophoric materials and their components

The values of p_0 and θ for excitation wavelengths of 280 nm and 365 nm are presented in Table I. The angles presented in column θ are the angles between the emission oscillator and the absorption oscillator, for pure solutions of the acceptor (DMP), of the pure donor (PT) and for the solution of bichromophoric material, respectively, the symbols are θ_A , θ_D and θ_{DA} , respectively.

The above data allow us to observe in the long wavelength absorption band, absorption and emission oscillators, closing a small angle ($\theta_A \approx \theta_{DA} \approx 10^\circ$) with each other, and lying presumably along the longitudinal axis of the molecule can belong to the pure acceptor and acceptor-part of bichromophoric molecule, respectively. The angle closed by the absorption and emission oscillators of the donor (PT) is $\theta_D \approx 18$ degrees, their direction are roughly that of the longitudinal axis of the donor [17].

If the energy transfer is considered as being of the Förster type in respect of our assumption that the energy transfer should place between the emission oscillator of the donor-part and the absorption oscillator of the acceptor-part then, on the evidence of the data the angle θ_{DA} closed by these in the PT-CH₂-DMP is approximately 68 degrees, in the PT-CH₂-S-CH₂-DMP it is smaller, approximately 59 degrees (Fig. 5).

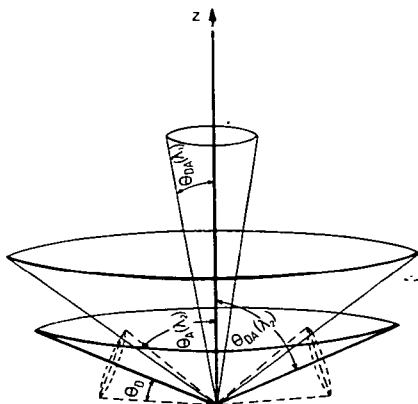


Fig. 5. The settlement of the absorption and emission oscillators of the bichromophoric molecule PT-CH₂-DMP at exciting wavelengths of $\lambda_1 = 365$ nm and $\lambda_2 = 280$ nm. The emission oscillator of the acceptor-part points in the direction of the z axis. $\theta_{DA}(\lambda_1)$ and $\theta_A(\lambda_2)$ and $\theta_{DA}(\lambda_2)$, respectively, are the angles between the absorption oscillators ordered to the transition $S_0^A \rightarrow S_1^A$ of the acceptor-part and to the transition $S_0^A \rightarrow S_2^A$ of the acceptor as well as between the absorption oscillator of the donor part and the z axis. θ_D is the angle between the absorption and emission oscillators of the donor.

On the basis of Eq. (1), the value of R_0 was determined supposing that $\kappa = 1$. $R_0 = 4.65$ nm for solutions in dioxane, $R_0 = 4.67$ nm for solutions in cyclohexane. In spite of the above value of R_0 if the estimated distance of the molecule moieties is 0.5-1.2 nm, the efficiency of the energy transfer may be high even for a high value of θ_{DA} . However, Förster's consideration can not be used with any precision in a zone so near and the determination the orientation factor κ has practically no sense from the aspect of physics, only the θ angles have got such sense.

7. The experimental results described above can be summarized in the following:

a) The absorption coefficients of the solutions of the bichromophoric materials agree with an almost correct estimate with the absorption coefficients which can be ordered to the constituent materials, in spite of the fact that there is a strong interaction between the donor and acceptor molecule-parts, in consequence of which the donor \rightarrow acceptor energy transfer takes place in much shorter time than one ns.

b) According to the result of a detailed examination of deviations from the above-mentioned additivity, it is the absorption of the donor-part that undergoes the greater change, and this change is practically equivalent to the appearance of a new absorption band.

c) When comparing the emission spectra of the solutions of the bichromophoric materials with the fluorescence spectra of the constituents, it becomes evident that the emission spectrum of the bichromophores is almost identical with that of the acceptor. The maximum of the remaining weak fluorescence band of the donor is less than two per cent of the maximum of the fluorescence spectrum of the bichromophore.

d) The connection between absorption and emission spectra was examined in detail. The effective temperature which may be ordered to the acceptor and the bichromophore, respectively, was also established and it was generally found to be bit slightly different from the experimental temperature.

A perceptible change has been found in PT-CH₂-S-CH₂-DMP solved in cyclohexane. With this solution, a higher effective temperature corresponds to a higher exciting photon energy.

e) With a method reported by our institute, we determined the long-wavelength pure electron transition frequency ν_0 of the acceptor and of the acceptor-part of the bichromophore, by using the absorption and emission spectra of the materials concerned. The decay time of the fluorescence of the pure acceptor and of the bichromophoric solutions was calculated by using the volume of ν_0 and the absolute quantum yield, on basis of Strickler-Berg's formula. The decay times were also determined experimentally, with an accuracy of about two per cent; these showed a surprisingly good agreement with the calculated time. This agreement is all the more interesting, as the luminescence characteristics of the solutions of the bichromophoric materials do not correspond even approximately to the assumptions used for the derivation from Strickler—Berg's formula.

f) The yield of the donor and acceptor materials are approximately in agreement and the yield of the solution of the bichromophoric materials coincide approximately with these. The anti-Stokes yield dropping can be observed.

g) The fundamental polarisation spectra of the donor, acceptor and solutions of the bichromophoric materials were recorded. Statements have been taken concerning the orientation of the oscillators. Further examinations are required to decide what kind of connection is to be found between the direction of the oscillators and the spatial structure of molecules.

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ВНУТРИМОЛЕКУЛЯРНОЙ ЭНЕРГЕТИЧЕСКИЙ ТРАНСФЕР В БИХРОМОФОРНЫХ МОЛЕКУЛАХ

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Даны результаты изучения двух лазер-активных бихромофорных красителей. Были определены частоты переходов красителей между состояниями $S_0 \rightarrow S_1$ и их времена жизни. Были сняты спектры фундаментальной поляризации и определены углы между осцилляторами поглощения и испускания.