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FLUORESCENCE AND LASER PARAMETERS OF THREE NEW ANTHRACENE DERIVATIVES[*, **]

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The fluorescence parameters important for stimulated emission of 9,10-diphenylanthracene (I), 10-phenyl-9-acetoxyanthracene (II), 10-(4-acetoxyphenyl)-9-acetoxyanthracene (III) and 10-(4-methylphenyl)-9-acetoxyanthracene (IV) are determined for toluene and dioxane solutions. For all those compounds the lasing action has been confirmed. The gain of the compounds has been measured. The measured and calculated gain spectrum for 9,10-diphenyl-anthracene shows good coincidence when in the calculations the triplet absorption losses are taken into account.

1. *Introduction*

It has been known [1] that some of the anthracene derivatives, e.g. 9,10-diphenylanthracene, 9-phenylanthracene, 9- and 9,10-dimethylanthracene and 9-chloroanthracene show laser emission in organic solutions at low and room temperature. Recently, Gronowska [2] synthesized many compounds, derivatives of 9-acetoxyanthracene. The absorption and emission spectra, the quantum yield Q_f and the lifetime τ_f of fluorescence of these compounds in n-heptane were investigated in our earlier work [3]. It follows from these experimental studies that the fluorescence quantum yield of some compounds is sufficiently high in order to get lasing action. Also, the maximal value of the intersystem crossing rate, $k_{S_1T_1}$, estimated by using the obtained fluorescence parameters Q_f and τ_f ($k_{S_1T_1}$ is 2.5 times smaller than that for anthracene [4]), indicates that these compounds can be applied as active medium in dye lasers.

In the present work an observation is reported of lasing action in 10-phenyl-9-acetoxyanthracene (II), 10-(4-acetoxyphenyl)-9-acetoxyanthracene (III), and 10-(4-methyl-phenyl)-9-acetoxyanthracene (IV) which were dissolved in dioxane and toluene. The lasing properties of those compounds are compared with the data obtained for 9,10-diphenylanthracene (I) for which the laser action was obtained for the first time by Myer et al. [5].

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2. Experimental

The experimental setup used for this study consists of two different facilities: the fluorescence-spectroscopy and gain-spectroscopy arrangements. The fluorescence-spectroscopy apparatus for emission spectra and quantum yield measurements is an improved version of the experimental setup described in our earlier work [3]. The apparatus for measuring the fluorescence quantum yield was calibrated by means of anthracene solution in n-hexane [6] and 9,10-diphenyl-anthracene in benzene [7] for which the fluorescence quantum yield is well known. The absorption spectra were measured on the Perkin-Elmer Type 402 and Zeiss-Jena type VSU-2 spectrophotometers.

The fluorescence lifetime measurements for the toluene and dioxane solutions of those compounds were performed by means of the phase shift fluorometer [8]. In the apparatus solutions are excited with a HBO-200 mercury lamp through a monochromator transmitting the 365 nm Hg I line. The emission was observed through a second monochromator at the wavelength which corrcsponds to the first vibration peak of the emission spectrum.

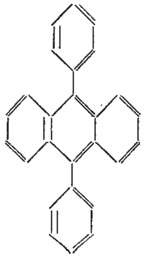
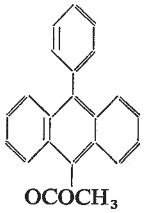
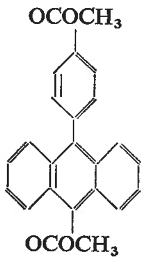
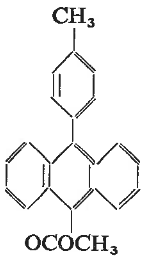
Table I shows the determined luminescence parameters of the investigated compounds. Here the structural formulae are also given. The quantum yield and decay time of the solutions were measured several times. The figures given in Table I are the average values of five measurements performed at intervals of several days. The instrumental errors of the decay lifetime and the quantum yield are ±0.1 ns and ±0.05, respectively.

For example the spectroscopic data important for laser action in 9,10-diphenylanthracene in dioxane solution at room temperature are graphically shown in Fig. 2. The absorption and emission cross sections are determined on the basis of measured absorption and emission spectra, fluorescence quantum yield and decay lifetime of fluorescence. The coefficient of the $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ absorption are taken from Langelaar's paper [9]. For these absorption spectra, the shift of intensity peaks caused by the solvent was taken into account. Fig. 2 shows a complete overlap of the emission cross section and the triplet absorption spectrum. One can expect that this kind of overlapping spectra will be also found for the other investigated compounds. It has to be noted that the $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ absorption spectra for the II, III and IV compounds are not known.

The simplified scheme of the gain-spectroscopy arrangement is shown in Fig. 1. This apparatus consists of self-built N_2 laser giving output pulses of ~10 ns duration with peak intensity of 350 kW, cooling pumping circule of the dye solution, monochromator and light detecting systems. The gain cell is transversely pumped by the N_2 laser whose radiation was focused by means of cylindrical lens. The shutter alternately exposed 1.1 or 0.55 cm segments of the cell. The amplified spontaneous emission for a given wavelength filtered by means of the grating monochromator is registered by the X-T recorder. An aperture is placed between the monochromator and the dye cell to ensure that all of the collected light has passed through the pumped region. The aperture is placed far enough from the sample cell so that the detector-cell spacing is many times larger compared to the length of the pumped region.

TABLE I

Determined luminescence parameters of the investigated anthracene derivatives

Compound	Solvent	Quantum yield Q_f	Decay time τ_f [ns]	$k^{\max}_{S_1T_1} \times 10^7$ [s^{-1}]
9,10-diphenyl-anthracene (I) — DPA 	toluene dioxane	0.77 0.95	5.85 6.70	3.93 0.75
10-phenyl-9-acetoxy-anthracene (II) — PAcA 	toluene dioxane	0.82 0.99	6.35 8.50	2.84 0.11
10-(4-acetoxyphenyl) -9-acetoxyanthracene (III) -10 (4AcP)9AcA 	toluene dioxane	0.75 0.87	6.35 7.75	3.94 1.67
10-(4-methylphenyl)- -9-acetoxyanthracene (IV) -10(4CH$_3$P)9AcA 	toluene dioxane	0.74 0.87	6.30 8.05	4.12 1.61

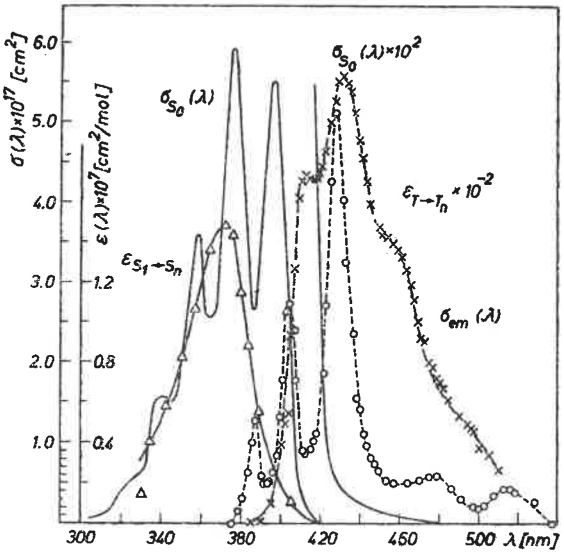


Fig. 1. Determined absorption (———) and emission (—×—) cross sections, and $S_1 \rightarrow S_n$(—Δ—) and $T_1 \rightarrow T_n$ (-○-○-) absorption spectra of 9,10-diphenylanthracene in dioxane solutions

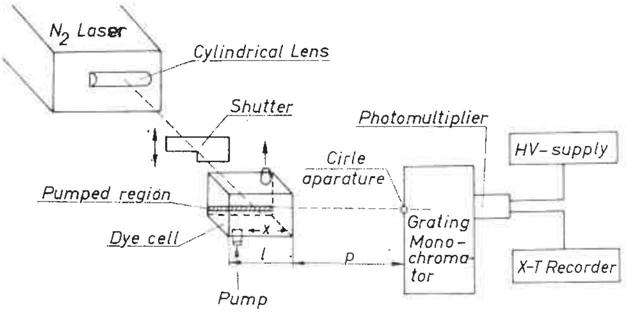


Fig. 2. Scheme of the experimental set up

Fig. 3 shows recordings of the amplified spontaneous fluorescence intensity detected when the half ($I_{l/2}$) and whole (I_l) length of the sample cell is pumped. In order to eliminate any error due to nonuniform pumping of the N_2 laser, the intensity curve of $I_{l/2}$ in Fig. 3 is presented as an average. The average curve has been obtained from curves when left and right half length is pumped. For the investigated dyes no saturation was observed using full radiation of the N_2 laser focused by a cylindrical lens ($f = 10$ cm) on the total cell ($l = 1.1$ cm) [4].

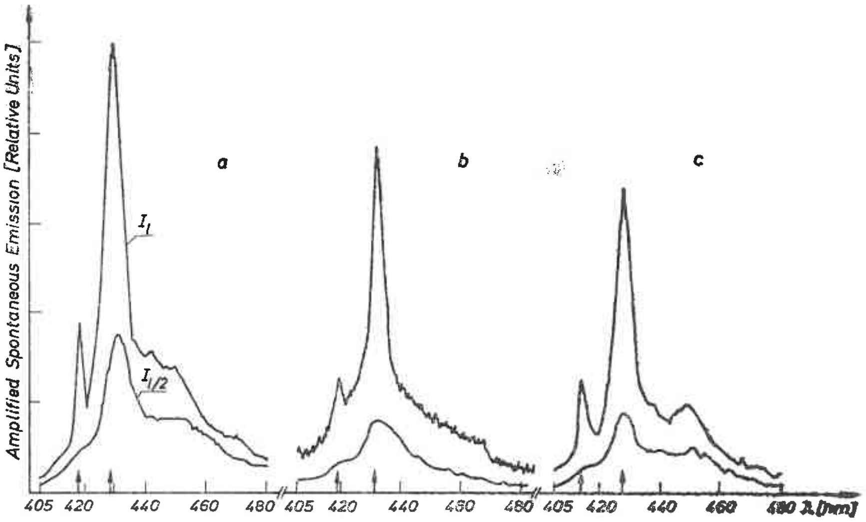


Fig. 3. Measured amplified spontaneous fluorescence of: a) 10-phenyl-9-acetoxyanthracene ($c = 5.10^{-2}$ M), b) 9,10-diphenyl-anthracene ($c = 1.10^{-3}$ M), and c) 10-(4-acetoxyphenyl)-9-acetoxyanthracene ($c = 5.10^{-2}$ M) in dioxane solutions

3. Discussion and conclusions

Analyzing the fluorescence parameters collected in Table I it can be seen that the fluorescence quantum yield in dioxane has the bigger value than that obtained in toluene. Also, the decay lifetimes are longer in dioxane solutions. This behavior is true for all compounds. Significant differences between the Q_f and τ_f values are of the same order. It means that ratios Q_f^{toluene} to Q_f^{dioxane} and τ_f^{toluene} to τ_f^{dioxane} are equal in the error limit. Substituting equations which define the Q_f and τ_f parameters [10] one will get the sum of radiationless transition probabilities depopulating the S_1 state:

$$k_{S_1T_1} + W_{S_1S_0} = \frac{1-Q_f}{\tau_f}, \tag{1}$$

where $W_{S_1S_0}$ is the probability of internal non radiative $S_1 \to S_0$ transition and $k_{S_1T_1}$ is the intersytem crossing constant.

The data obtained from our measurements are given in the last column of Table I. The value of the sum of radiationless transition probability shows a contrary dependence to that observed for the quantum yield and decay lifetime. Also, the values of $k_{S_1T_1} + W_{S_1S_0}$ can be treated as the upper limit of the intersystem crossing constant $k_{S_1T_1}^{\max}$ if $W_{S_1S_0}$ was small and could be disregarded. Treating the numbers given in the last column of Table I as $k_{S_1T_1}^{\max}$ and comparing them with the value for anthracene (0.23×10^8 s [11]) one will see that they differ by one order. This high value of $k_{S_1T_1}$ frustrates lasing action in anthracene solutions.

On the basis of the amplified spontaneous emission spectra (see Fig. 3), applying the formula [12]:

$$G(\lambda) = \frac{2}{l}\ln(I_l/I_{l/2}-1) \tag{2}$$

one can determine the gain $G(\lambda)$. In Eq. (2) l is the full length of the pumped region, I_l and $I_{l/2}$ is the fluorescence intensity of the full cell and the average from each half of the cell, respectively. Table II contains the obtained $G(\lambda)$ values for the short- and longwave maximum. The estimated error for the obtained gain values equals about 15%. As it follows from the data assembled in Table II the values of $G(\lambda)$ of the shortwave maximum are equal in the error limit for all dyes. The $G(\lambda)$ values of the longwave maximum reaches the highest value ($G(\lambda) = 2.90\ \mathrm{cm}^{-1}$) for 9,10-diphenylanthracene. The $G(\lambda)$ value of 10-phenyl-9-acetoxyanthracene is 25 per cent and for 10-(4-acetoxyphenyl)-9-acetoxy anthracene and 10-(4-methylphenyl)-9-acetoxyanthracene 48 per cent smaller than for 9,10-diphenylanthracene. Only small changes in the wavelength of $G(\lambda)$ maxima are observed. It suggests that the positions of the triplet absorption maxima of those compounds show only insignificant wavelength change.

TABLE II

Determined gain values of the investigated anthracene derivatives

Compound	DPA (I)	PAcA (II)	10(4AcP)9AcA (III)	10($4CH_3$P)9AcA (IV)
Concentration	1.10^{-3} M	5.10^{-2} M	5.10^{-2} M	5.10^{-2} M
λ of shortwave maximum [nm]	419.0	414.0	417.7	—
$G(\lambda)$ [cm^{-1}]	2.55	2.48	2.58	—
λ of longwave maximum [nm]	432.0	427.5	428.3	431.0
$G(\lambda)$ [cm^{-1}]	2.90	2.16	1.52	1.51

The gain spectrum, as it follows from Fig. 3, shows discrete structure. This is due to the overlapping of stimulated emission spectrum and the frequency-dependent losses such as the triplet and the excited-state absorption. The theoretical description of a dye laser [13] for the measured gain of a dye solution leads to formula:

$$G(\lambda) = \frac{\lambda^4 E(\lambda)}{8\pi c\eta^2\tau_f} N_{S_1} - \sigma_{S_0}(\lambda)N_{S_0} - \varepsilon(\lambda). \tag{3}$$

Here $G(\lambda)$ is given in inverse centimeters, $E(\lambda)$ is the true fluorescence line shape normalized so that $\int_0^\infty E(\lambda)d\lambda = Q_f$, τ_f is the decay lifetime and η is the index of refraction. N_{S_1} and N_{S_0} are the excited singlet and ground state population densities, respectively, and $\sigma_{S_0}(\lambda)$ is the singlet absorption cross section. The quantity $\varepsilon(\lambda)$ represents triplet and singlet excited state absorption losses.

Fig. 4 shows the measured (triangles) and calculated (points and circles) gain spectrum of 9,10-diphenylanthracene 1×10^{-3} M solution in dioxane. The calculations are based on cross sections which are graphically shown in Fig. 2. The circles have been obtained by using two first terms of Eq. (3) only. The fractional population density of the excited singlet population N_{S_1}/N_{S_0} was used as a free fitting parameter and was determined to be equal to 0.08. It can be seen in Fig. 4 that the circles do not follow the experimental gain spectrum. This disagreement is probably due to the triplet absorption losses. Considering this fact, the gain for 9,10-diphenylanthracene have been calculated by using three terms of Eq. (3). In the last calculation the ratio of $N_{S_1}/N_{S_0} = 0.08$. N_{T_1} was used as a free fitting parameter.

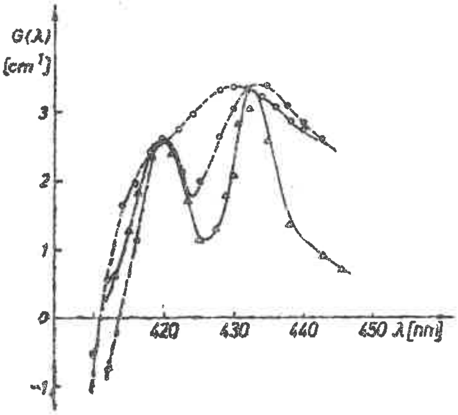


Fig. 4. Experimental gain spectrum of 9,10-diphenylanthracene ($c = 1.10^{-3}$ M) in dioxane and calculated gain spectrum obtained disregarding (–●–●–) and taking into account (–○–○–) the $T_1 \rightarrow T_n$ absorption losses

The $G(\lambda)$ values obtained in that way by using $N_{T_1} = 3.11 \times 10^{15}$ molecules per cm^3, and $\varepsilon(\lambda)$ values taken from Fig. 2, are represented by circles on Fig. 4. The curve given by the circles agrees qualitatively with the experimental one. It follows from qualitative agreement that laser action of those anthracene derivatives is influenced by frequency-dependent losses such as triplet absorption. It happens in those compounds also when for pump excitation 10 ns pulses of the N_2 laser are used.

Basing on the above results we constructed a simple broad band dye N_2 laser of the Hänsch type [14]. Using our 350 kW N_2 laser as pump source of the dye the stimulated emission was obtained only in 3.5 nm wide peak. The peak's wavelength of generated radiation is in accordance with the longer wavelength maximum of the amplified spontaneous emission spectrum. The spectrum of generated radiation for all compounds shows similar structure. It should be mentioned that the investigated dyes show photochemical degradation.

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