The $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ Absorption Spectra of Some Anthracene Derivatives

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A method for the determination of excited state absorption cross section spectra with a laser flash spectrometer is demonstrated. In the region 405 – 660 nm the cross sections of seven aromatic compounds in not degased dioxan at room temperature have been determined. The data obtained for anthracene are compared with those of other authors.

1. Introduction

The derivatives of 9-acetoxy-10-phenylanthracene possess interesting spectroscopic and laser properties [1 – 6]. The spectroscopic studies have shown that the nuclear conformation of the ground (S_0) and first excited (S_1) states are different. This is due to the steric effects of the substituents ($-OCOCH_3$ ($-OAc$); $-OCH_3$ ($-OMe$); $-CH_3$ ($-Me$) and $-C_6H_5$ ($-Ph$)) interacting with the π-electrons of the anthracene skeleton. Those substituents also cause the bathochromic effect of the ${}^1A_{1g} \rightarrow {}^1B_{2u}$ (${}^1A \rightarrow {}^1L_a$), ${}^1A_{1g} \rightarrow {}^1B_{1u}$ (${}^1A \rightarrow {}^1B_b$), ${}^1A_{1g} \rightarrow {}^1A_{1g}$ (${}^1A \rightarrow {}^1C_b$) bands, change the intensities in comparison with the parent compound and influence the fluorescence and radiationless rate constants.

The gain and laser output spectra, the absorption threshold and the amplified spontaneous emission depend on the position and kind of substituent. It follows from many papers [5 – 8] that those findings can be explained by the $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ absorption and the energy difference between the S_1 and T_1 levels.

For this reason, it was interesting to measure the absorption spectra originating from excited electric states. Results of these measurements will show excited molecular states not seen by one-step state absorption and give some experimental data needed to discuss the laser behavior of the studied derivatives of 9-acetoxy-10-phenylanthracene [4 – 6]. In this paper we will describe the laser absorption spectrometer constructed by us and give the results of absorption measurements on six derivatives of anthracene. The $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ absorption spectra of those compounds were obtained for the first time. The structure formula of the studied compounds with some spectroscopic parameters useful in the discussion (taken from our earlier measurements [1, 2, 4, 6]) are given in Table 1.

2. Experimental

2.1. Apparatus

Experimentalists have applied several methods to measure excited state, $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$, absorption spectra [9 – 14]. All of them use a flashing light source preexciting the sample and a second light source to measure timely delayed the absorption. These two light sources can work in a collinear [9 – 12] or in a crossed-beam [12 – 14] arrangement. Synchronization between the pumping and analysing light source is a critical aspect of this experiment. Pulsed lasers allowed to overcome those difficulties and improved the time resolution by many orders.

Figure 1 shows a diagram of our apparatus. The spectrometer consists of an N_2 preexcitation laser a second synchronous N_2 pumped dye laser, a variable optical delay line and a light detecting system. The N_2 pumped dye laser worked in a Hänsch arrangement. The generated light is tuned by a prism and by a Bausch & Lomb grating (1800 grooves/mm, 0.1 nm resolution). The end mirror ($R = 2$ m) of the dye laser had a transmission of 30 – 40% for the spectral region of interest. The output energy and the pulse duration (fwhm) of the nitrogen laser are equal to 450 kW and 2.5 ns, respectively. As active

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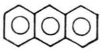
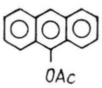
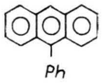
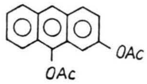
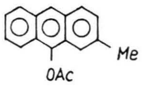
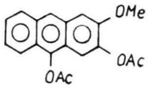
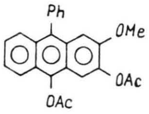
Table 1. The fluorescence decay time τ_F and $\gamma_{S_1} = \tau_F^{-1}$; quantum yield Q_F and the fluorescence, k_F, and radiationless process, k_D, rate constants. The absorption cross sections for $\lambda = 337.1$ nm are also given.

	Compound	Q_F	τ_F [ns] $\gamma_{S_1} \times 10^8$ [s^{-1}]	$k_F \times 10^7$ [s^{-1}]	$k_D \times 10^7$ [s^{-1}] Q_D	$\sigma_{S_0}(337.1)$ $\times 10^{-17}$ [cm^2]
I		0.33	4.6 2.17	7.2	14.6 0.67	1.50
II		0.21	4.2 2.38	5.0	19.0 0.79	0.97
III		0.51	6.5 1.52	7.8	7.5 0.49	0.97
IV		0.41	8.1 1.23	5.1	7.3 0.59	1.15
V		0.34	7.2 1.39	4.7	9.2 0.66	1.20
VI		0.62	12.1 0.82	5.1	3.1 0.38	1.48
VII		0.73	9.8 1.02	7.4	2.7 0.27	1.46

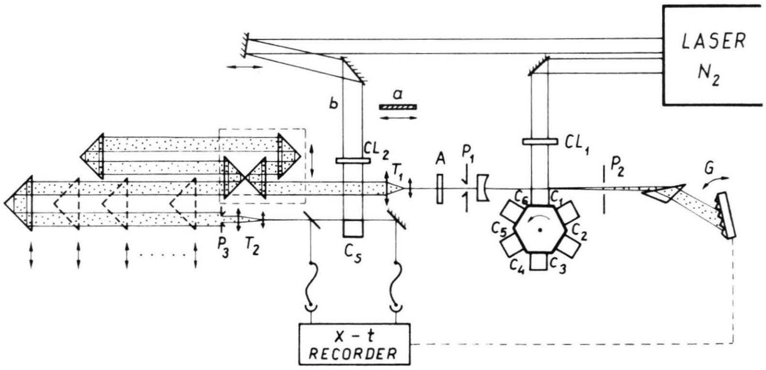


Fig. 1. The experimental set-up. G diffraction grating, $P_1 \dots P_3$ pin holes; A optical density filter; CL_1, CL_2 cylindrical lenses; T_1, T_2 beam expanding telescopes; $C_1 \dots C_5$ dye laser cells on a rotary holder; C_s dye cell of the studied compound.

lasing media ethyl alcohol solutions of stilben 3 (405–456 nm), coumarine 480 (450–515 nm), coumarine 540 (510–580 nm), rhodamine 590 (575–625 nm) and rhodamine 640 (620–660 nm), where used (dye concentration $2-9 \cdot 10^{-3}$ Mol/l, depending on the dye). The dye cells are set up on a rotary stand coupled with the diffraction grating. The dye laser beam was expanded by a telescope in order to get a proper dimension and reduced divergence of the beam throughout the delay line, which gives retardations from 2 to 40 ns. In the cell the analysing light beam has a diameter of $D = 0.1$ mm.

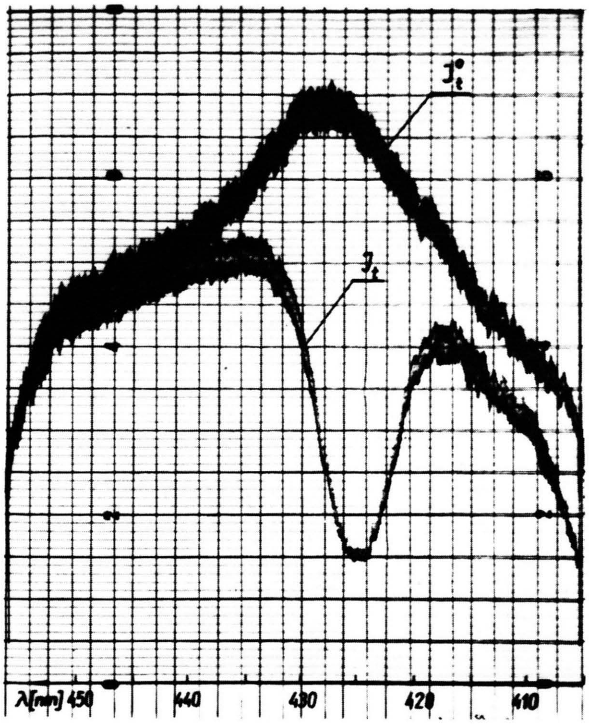


Fig. 2. Examplified recording of the $T_1 \rightarrow T_n$ absorption for anthracene in dioxane solution. I_t, I_t^0 transmission spectra with and without excitation.

The beam intensity was detected twice: By the first photomultiplier to have a reference signal and by the second photomultiplier to measure the cell absorption. Both integrated electric signals were registered with an X–t recorder. The neutral filter A prevents an overloading of the photomultipliers. Figure 2 shows a typical recording of the analysing beam transmission without and with preexcitation.

2.2. *Principle of Measuring Procedure*

Figure 3 shows a detailed drawing of the crossed-beam setup used in the $S_1 \rightarrow S_n$, $T_1 \rightarrow T_n$ absorption measurements.

In order to determine the absorption cross section spectra of the $S_1 \rightarrow S_n$, $T_1 \rightarrow T_n$ transition two absorption measurements are necessary: One for a non preexcited sample and a second one for a sample preexcited by N_2 laser light. For dilute solutions (the Lambert-Beer law) the analysing light intensities are

$$I_t^0 = I_0 \exp(-\sigma_{S_0} N_{S_0} l) \tag{1}$$

and

$$I_t = I_0 \exp\left(-\sigma_{S_0} N_{S_0} l - \sigma_{S_1} l \,\frac{\int\limits_{t_0}^{t_0+\tau} N_{S_1}(t)\,\mathrm{d}t}{\tau} - \sigma_{T_1} l \,\frac{\int\limits_{t_0}^{t_0+\tau} N_{T_1}(t)\,\mathrm{d}t}{\tau}\right). \tag{2}$$

In (1) and (2) σ_{S_0}, σ_{S_1} and σ_{T_1} are the photon absorption cross sections of the S_0, S_1 and T_1 electronic states, respectively, l is the absorption length (length of the sample cell), t_0 the time delay between preexciting and analysing flash and τ the half width of the dye laser pulse.

If $\sigma_{T_1} \cong 0$ or $N_{T_1} \cong 0$ we get

$$A_{S_1}(\tilde{\nu}) = \frac{1}{2.303} \ln \frac{I_t^0(\tilde{\nu})}{I_t(\tilde{\nu})} = \frac{\sigma_{S_1}(\tilde{\nu})\, l}{2.303}\, \frac{\int\limits_{t_0}^{t_0+\tau} N_{S_1}(t)\,\mathrm{d}t}{\tau} \tag{3}$$

and if $\sigma_{S_1} \cong 0$ or $N_{S_1} \cong 0$

$$A_{T_1}(\tilde{\nu}) = \frac{\sigma_{T_1}(\tilde{\nu})\, l}{2.303}\, \frac{\int\limits_{t_0}^{t_0+\tau} N_{T}(t)\,\mathrm{d}t}{\tau} = \sigma_{T_1}(\tilde{\nu})\, l\, N_{T_1}^{\max}. \tag{4}$$

Equations (3) and (4) give the absorbances at a particular wavelength of the $S_1 \rightarrow S_n$ or $T_1 \rightarrow T_n$ transition, respectively. The premise of (3) or (4) (a proper t_0 value) is realized by the optical delay line.

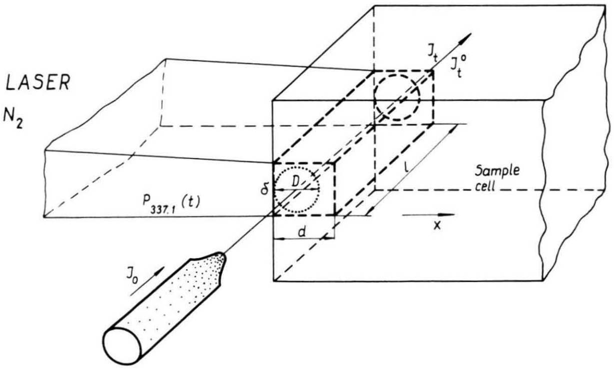


Fig. 3. Detailed drawing of the crossed-beam set-up in excited state absorption measurements. D diameter of analizing beam; d absorption depth for which $\sigma_{S_0}(337.1) \cdot N_{S_0} d = 1$; $l \times \delta$ the area excited by the N_2-laser.

In our case the excited-state S_1 and T_1 absorption measurements were performed for delay times $t_0 = 2$ and $t_0 \geqq 18$ ns, respectively. As is shown in Sect. 2.3, the selected delay times correspond to maximal population density in the S_1 or T_1. The average number of molecules in the S_1 state (taken over the whole pumping volume of the N_2 laser) is given by the formula

$$\bar{N}_{S_1} = a\,\sigma_{S_0}(337.1)\,N_{S_0} \int_0^D \int_0^{\tau_{N2}} q(x,t)\,dx\,dt\,, \qquad (5)$$

where a is a constant and $q(x,t)$ the photon density of the N_2 laser light in the excitation volume. If the Lambert-Beer law is fulfilled for the N_2 light penetrating the sample, (5) can be rewritten as

$$\bar{N}_{S_1} = \frac{a}{D\,\delta l}\,\sigma_{S_0}(337.1)\,N_{S_0} \cdot \int_0^D \int_0^{\tau_{N2}} P_{337.1}(t)\exp(-\sigma_{S_0} N_{S_0} x)\,dx\,dt\,. \qquad (6)$$

Equation (6), integrated over the absorption length, gives

$$\bar{N}_{S_1} = \frac{a}{D\,\delta l}\,[1-\exp(-\sigma_{S_0}(337.1)\,N_{S_0} D]\int_0^{\tau_{N2}} P_{337.1}(t)\,dt\,. \qquad (7)$$

The quantum yield of intersystem crossing after Amand and Bensasson [14] can be defined as

$$Q_{ISC} = \frac{\int_0^{t_{max}} dN_{T_1}}{\bar{N}_{S_1}}\,, \qquad (8)$$

where N_{T_1} describes the instantaneous population density of the molecules in the T_1 state and t_{max} is the time of assembling molecules in the T_1 state, counting them from the beginning of the excitation. Taking into account that $Q_{ISC} = 1 - Q_F$ and rewriting (3), (4), (7) and (8) for the case of the standard compound s (with known $\sigma^s_{T_1}$) and of the compound under studies x (unknown $\sigma^x_{T_1}$), after simple algebraic operations one gets

$$\sigma^x_{T_1} = \sigma^s_{T_1}\frac{A^x_{T_1}}{A^s_{T_1}}\frac{1-Q^s_F}{1-Q^x_F}\frac{1-\exp(-\sigma^s_{S_0}(337.1)\,N^s_{S_0} D)}{1-\exp(-\sigma^x_{S_0}(337.1)\,N^x_{S_0} D)}\,, \qquad (9)$$

$$\sigma^x_{S_1} = \sigma^s_{S_1}\frac{A^x_{S_1}}{A^s_{S_1}}\frac{1-\exp(-\sigma^s_{S_0}(337.1)\,N^s_{S_0} D)}{1-\exp(-\sigma^x_{S_0}(337.1)\,N^x_{S_0} D)}\,. \qquad (10)$$

Equation (10) is plausible for a case when the population rate constant is bigger than that of the depopulating processes of the S_1 state. It is easy to see that (9) and (10) allow to determine the absorption cross section spectra $\sigma^x_{T_1}$ and $\sigma^x_{S_1}$ without knowledge of the density of molecules in the S_1 and T_1 states.

It must be noticed that the absorption cross section spectra σ_{S_1} and σ_{T_1} can be determined also by means of (3) and (4) if the instant population density of the S_1 and T_1 states are known. These can be calculated by solving the rate equations for the population and depopulation dynamics of the S_1 and T_1 states. In this paper, the excited state absorbance spectra are determined in both ways.

2.3. Population Dynamics

The Jabłoński energy diagram of anthracene – the representative luminescence molecule of the studied compounds – is shown in Figure 4. In our experiment the S_1 ($v = 0$) state is populated through higher vibrational levels. Also, it would be possible to excite the molecules into the higher lying singlet states. But in this case, as well as if the higher vibrational levels of the S_1 state are excited, very fast thermalization takes place and all molecules quickly find themselves in the lowest vibronic level ($v = 0$) of S_1.

From the S_1 ($v = 0$) state the molecules lose excitation by spontaneous and stimulated emission and nonradiative intersystem crossings to the triplet state. In the measurements, by changing the pumping power of the N_2 laser, we took attention that amplified spontaneous emission was absent*. Taking only into consideration the processes described above, with rate constants $\gamma_{S_1} = 1/\tau_F$ and k_{ISC}, respectively, the population dynamics are controlled by the rate equation

$$\begin{bmatrix}\dot{N}_{S_1}\\ \dot{N}_{T_1}\\ \dot{N}_{S_0}\end{bmatrix} = \begin{bmatrix}-\gamma_{S_1} & 0 & W(t)\\ k_{ISC} & -\gamma_{T_1} & 0\\ \gamma_{S_1}-k_{ISC} & \gamma_{T_1} & -W(t)\end{bmatrix}\begin{bmatrix}N_{S_1}\\ N_{T_1}\\ N_{S_0}\end{bmatrix}, \qquad (11)$$

where the total density of the molecules is $N = N_{S_0} + N_{S_1} + N_{T_1}$ and γ_{T_1} is the overall decay rate of the T_1 state. The pumping rate is

$$W(t) = \frac{\sigma_{S_0}(337.1)}{\delta l\,d}\int_0^d P_{337.1}(t)\exp\left(-\frac{x}{d}\right)dx\,, \qquad (12)$$

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* The amplified spontaneous emission was observed by us for the 9-phenylanthracene only.

where the N_2 laser light absorption depth d is defined by the relation $\sigma_{S_0}(337.1)\,N_{S_0}\,d = 1$. The meaning of the other parameters (δ, l, D and x) is given in Figure 3.

The shape function of the N_2 laser pumping pulse is described by the formula

$$P_{N_2}(t) = \frac{P_{337.1}(t)}{\delta\, l} = \varrho\,[\exp(-k_1^P t) - \exp(-k_2^P t)]. \tag{13}$$

The photon density in the incident beam and the shape parameters k_1^P and k_2^P have constant values for a given laser. In our studies the parameters k_1^P and k_2^P were determined experimentally by a least squares fit procedure. The parameter ϱ has been obtained by adjusting the absorbances $A_{T_1}^{\max}$, using (4) and (11), with that of our measurements for anthracene in benzene as a standard. It appears that $\varrho = 13.18 \times 10^{23}$ [photon cm^{-2} s^{-1}], $k_1^P = 4 \times 10^8$ [s^{-1}] and $k_2^P = 4 \times 10^9$ [s^{-1}]. For the rate constant γ_{T_1} we used the value $\gamma_{T_1} = 6.0 \times 10^6$ [s^{-1}] obtained for anthracene [15].

Substituting the values of the spectroscopic parameters (see Table 1) and the value of the pumping rate into (11), the temporary population densities of the S_1, T_1 and S_0 states were computed. The calculations were performed by means of the method described in [16]. In those calculations the population density of the ground state S_0 was approximated by the formula

$$N_{S_0}(t) = N\left(1 - \int W(t)\,dt\right).$$

Figure 4 shows a graphical presentation of the results obtained for anthracene (I) and 2,9-diacetoxy-3-methoxy-anthracene (VI). The density curves of the remaining compounds have an analogue course. It is obvious that the population density depends on the dye concentration and on the kind of solvent [17].

3. Results and Discussion

The absorption measurements on the excited species were performed at wavenumber intervals of 350 cm^{-1} in the region 15–24.5 kK (660–410 nm). Figures 5–7 show the absorption (σ_{S_0}) and stimulated emission (σ_e) cross-section spectra and excited singlet A_{S_1} and excited triplet A_{T_1} absorbances of the studied compounds in dioxane solution at room temperature. The excited singlet and triplet absorbance spectra were measured at the times $t_0 = 2$ ns and $t_0 \gg 18$ ns after the start of the preexciting laser pulse, respectively. The absorption and stimulated emission spectra give the strength of an absorption process and the number of fluorescence quanta per wave number interval.

The values of stimulated emission cross section have been calculated using the formula

$$\sigma_e(\tilde{\nu}) = \frac{g(\tilde{\nu})\,Q_F}{8\pi c\, n^2\, \tau_F\, \tilde{\nu}^2}, \tag{14}$$

where for the fluorescence shape function: $\int_0^\infty g(\tilde{\nu})\,d\tilde{\nu} = 1$. Q_F is the quantum yield, n the refraction index of the solution and τ_F the fluorescence mean decay time.

The absorbance spectra $A_{S_1}(\tilde{\nu})$ and $A_{T_1}(\tilde{\nu})$ are obtained as defined in (3) and (4).

The absorption cross section spectra σ_{S_0} of the substituted compounds are similar in shape and intensity to the spectra of the unsubstituted anthracene. They are shifted to longer wave lengths. This general similarity allows to use the symmetry assignment of anthracene for the electronic states (bands) although the substituted molecules belong no longer to the symmetry group D_{2h}. Substitution in position 9 of the anthracene ring causes a change in the electric transition moments parallel to the shorter axis of the molecule. They give rise to shifts and intensity changes of the following bands:

$$S_0(^1A_{1g}) \rightarrow S_1(^1B_{2u}) \quad (\sim 26700\ \mathrm{cm}^{-1}),$$
$$S_1(^1B_{2u}) \rightarrow S_n(^1A_{1g}) \quad (\sim 16650\ \mathrm{cm}^{-1}) \quad \text{and}$$
$$S_1(^1B_{2u}) \rightarrow S_k(^1B_{1g}) \quad (\sim 18000\ \mathrm{cm}^{-1}).$$

As it can be seen from Figs. 5, 6 and 7, the intensities of the vibrational peaks as well as the total intensity change slightly. In the case of the $S_0(^1A_{1g}) \rightarrow S_1(^1B_{2u})$ band the frequency differences between neighbouring vibrational peaks for the compounds II–VI are the same and are equal to those of anthracene. But for 9-phenylanthracene these differences are significantly larger than the experimental error. The excited state absorption spectra $S_1(^1B_{2u}) \rightarrow S_n(^1A_{1g})$ and $S_1(^1B_{2u}) \rightarrow S_k(^1B_{1g})$ have the same shape but the intensity decreases in comparison with those of anthracene.

Substitution of functional groups in positions 2 and 3 of the anthracene ring causes a change in the electric transition moment in the direction of the longer axis of the molecule. Among the observed

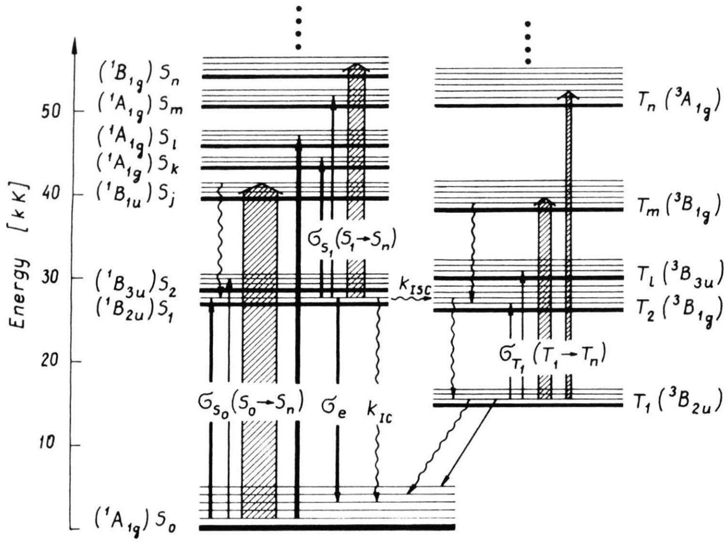


Fig. 4. The Jabłoński energy-level diagram of anthracene. The arrow width is proportional to the transition intensity.

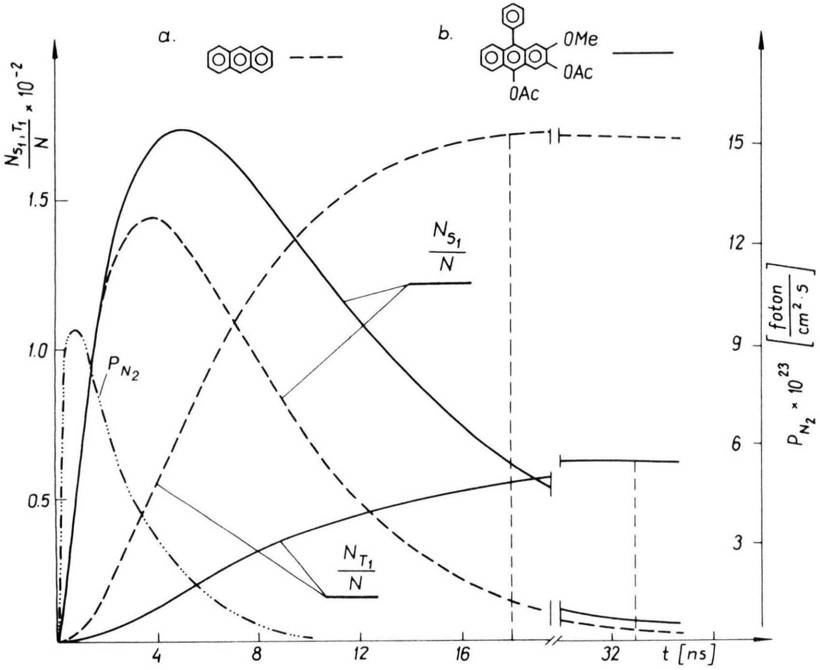


Fig. 5. The population density of the S_1 and T_1 states vs. time for anthracene (a) and 2,9-diacetoxy-3-methoxy-9-phenylanthracene (b). The pump laser pulse is given for comparison.

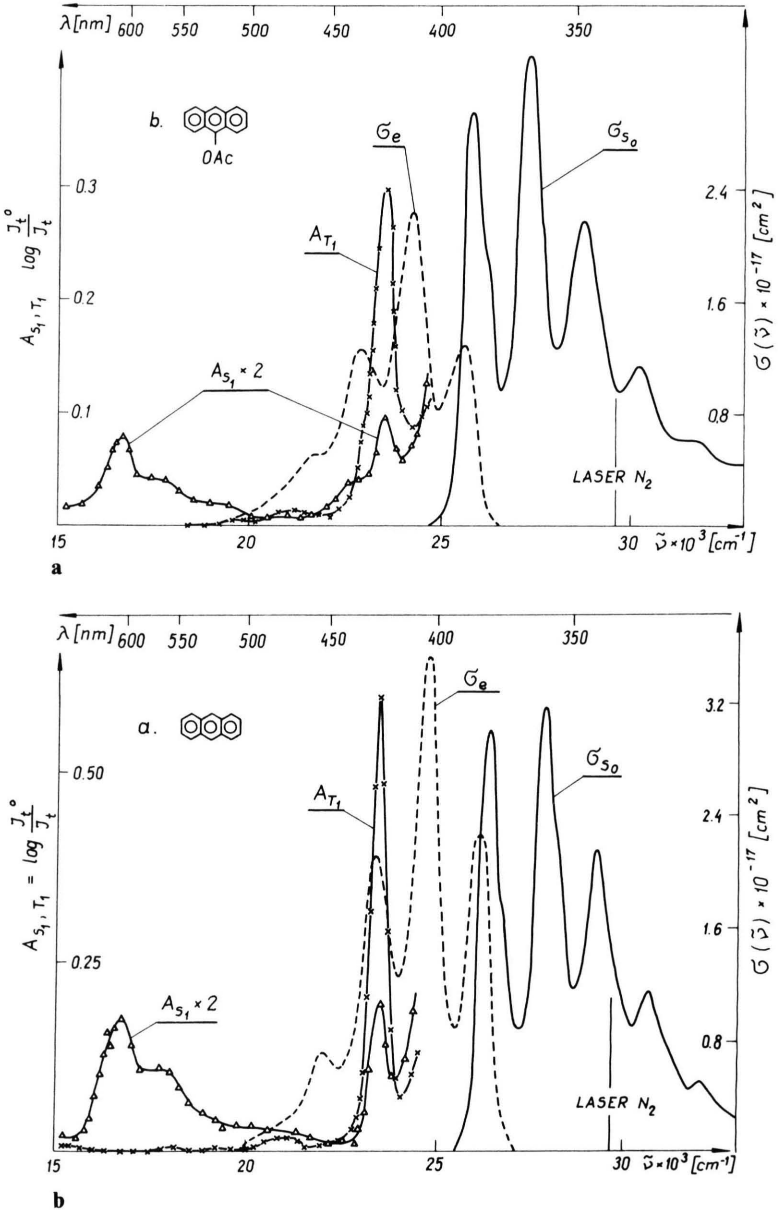
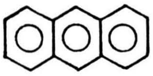
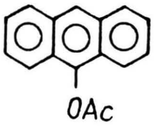
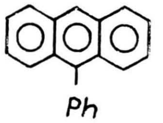
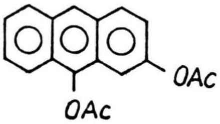
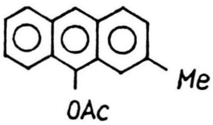
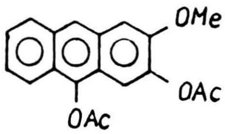
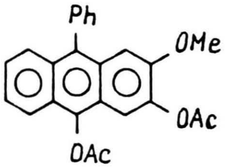


Fig. 6. The absorption spectra of anthracene (a) and 9-acetoxyanthracene (b) in dioxane solution at room temperature, $C = 3 \times 10^{-4}$ mol/l. ——— $\sigma_{S_0}(S_0 \to S_1)$; △—△—△ $A_{S_1}(S_1 \to S_n)$; ×—×—× A_{T_1} $(T_1 \to T_n)$. For convenience the stimulated emission cross section spectrum is also given.

Table 2. Frequencies of the absorption cross section vibration peaks and their values of the substituted derivatives of anthracene in dioxane. The values in paranthesis are calculated using (3) and (4). Here anthracene was applied as standard, for which $\sigma^{s}_{T_1} \cong 17.5 \times 10^{-17}$ cm^2 at 432.5 nm in benzene solution [18] and $\sigma^{s}_{S_1} \cong 3.84 \times 10^{-17}$ cm^2 at 16 700 cm^{-1} in PMM [19].

	Compounds	$S_0(^1A_{1g}) \rightarrow S_1(^1B_{2u})$		$S_1(^1B_{2u}) \rightarrow S_n(^1A_{1g})$		$T_1(^3B_{2u}) \rightarrow T_n(^3B_{1g})$	
		$\tilde{\nu}$ [cm^{-1}]	$\sigma_{S_0} \times 10^{-17}$ [cm^2]	$\tilde{\nu}$ [cm^{-1}]	$\sigma_{S_1} \times 10^{-17}$ [cm^2]	$\tilde{\nu}$ [cm^{-1}]	$\sigma_{T_1} \times 10^{-17}$ [cm^2]
I		26 420 27 830 29 250 30 710 32 080	2.02 3.18 2.18 1.19 0.54	16 650	3.80 (4.11)	23 490	25.0 (25.9)
II		25 830 27 210 28 710 30 170 31 500	3.06 3.37 2.22 1.19 0.61	16 650	2.69 (3.15)	23 540	14.7 (13.7)
III		25 800 27 200 28 650 30 100 31 700	3.28 3.49 2.16 1.08 0.51	16 750	3.95	23 000	8.3
IV		25 750 27 170 28 580 30 000 31 500	2.49 2.76 2.07 1.23	16 600	2.76 (2.77)	23 100	10.2 (13.0)
V		25 830 27 170 28 580 29 950 31 380	2.68 2.92 2.18 1.26 0.61	16 600	2.72 (2.67)	23 100	11.5 (10.08)
VI		25 500 26 960 28 290 29 750 31 250	2.18 2.26 2.15 1.53 0.84	16 900	3.98 (3.56)	22 730	10.2 (11.5)
VII		25 000 26 420 27 880 29 330 30 830	2.87 2.91 2.53 1.57 0.73	16 800	3.82 (3.49)	22 670	9.4 (9.72)

absorption bands only the transition moment of the $T_1(^3B_{2u}) \rightarrow T_n(^3B_{1g})$ (~ 23 500 cm^{-1}) band is parallel to the longer axis. As can be seen from Figs. 5, 6 and 7 for the substituted compounds (III–VII) this band shows a batchochromic shift. This frequence shift, calculated with respect to the anthracene value, is 400 cm^{-1} (compounds IV and V), 500 cm^{-1} (compound III) and 800 cm^{-1} (compound V), respectively. In the case of compound II this band shows a small shift to higher frequencies

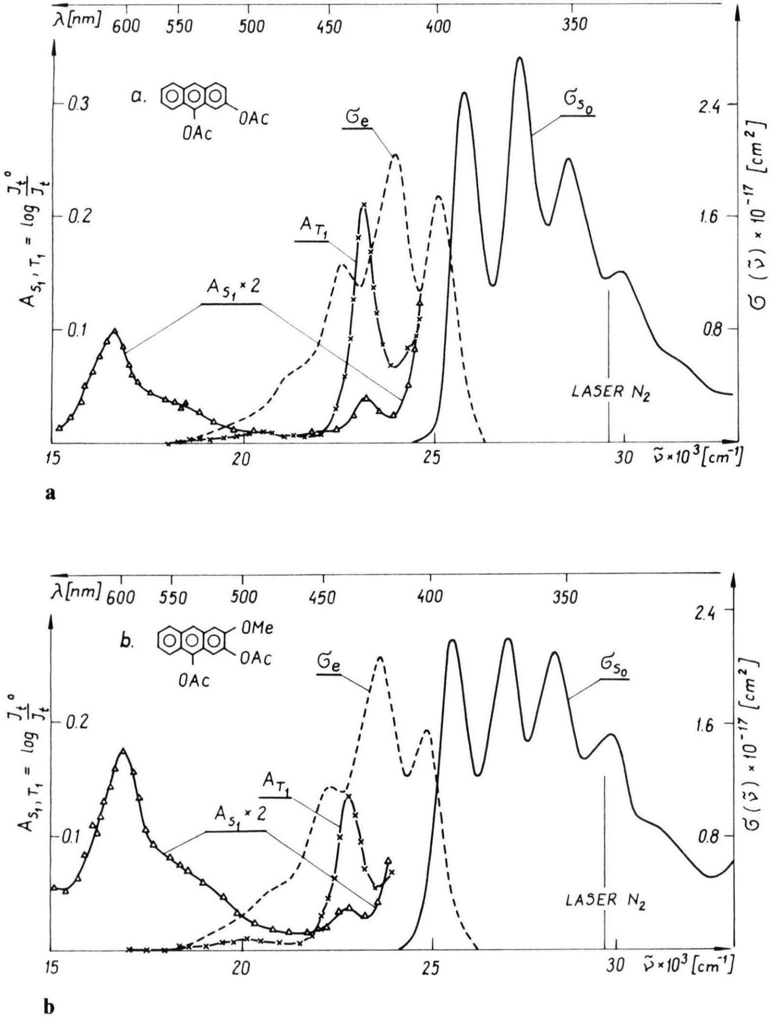


Fig. 7. The absorption spectra of 2,9-diacetoxy-anthracene (a) and 2,9-diacetoxy-3-methoxy-anthracene (b) in dioxane at room temperature. $C = 3 \times 10^{-4}$ mol/l. The spectra are marked as in Figure 6.

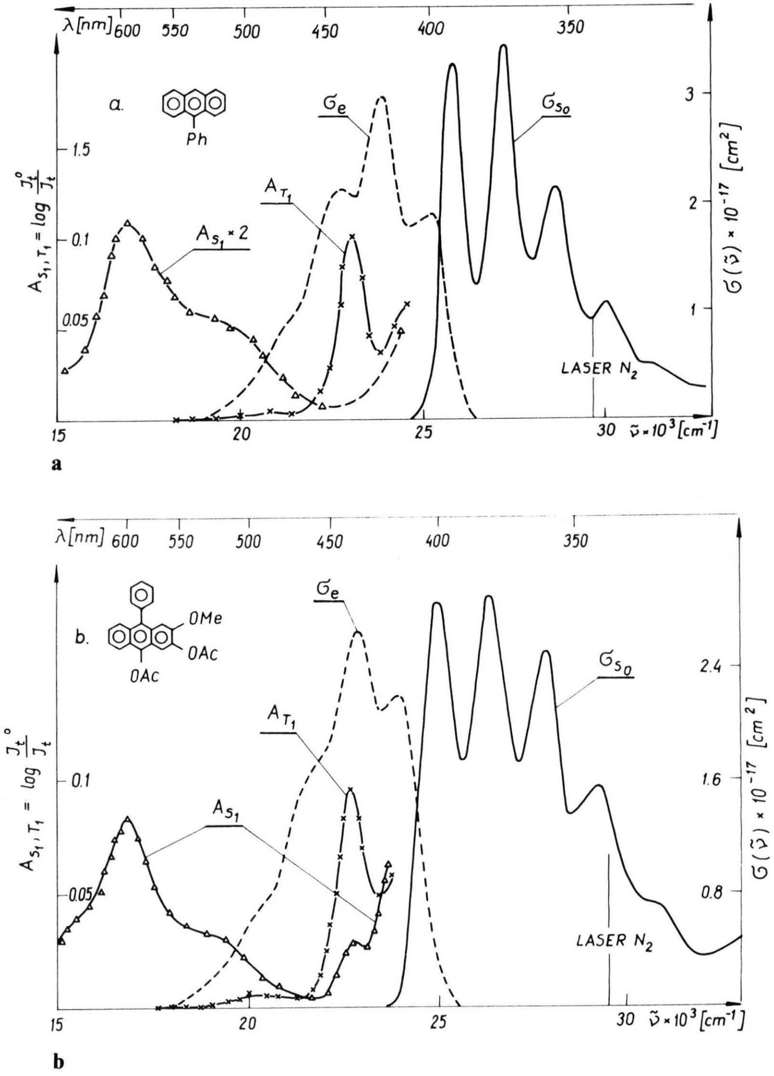


Fig. 8. The absorption cross section spectra of 9-phenylanthracene (a) and 2,9-diacetoxy-3-methoxy-10-phenylanthracene (b) in dioxane ($T = 293$ K, $C = 3 \times 10^{-4}$ mol/l). The spectra are marked as in Figure 6.

(hypsochromic effect). Additionally, to the $^3B_{2u} \rightarrow {}^3B_{1g}$ band in the delayed ($t_0 \geqq 18$ ns) spectrum a very weak peak at $\sim 21\,000$ cm^{-1} shows up. This peak appears in the spectra of all studied compounds.

Table 2 collects the wave numbers of the absorption maxima and their cross sections. The cross sections σ_{S_1} and σ_{T_1} were determined using (9) and (10) (upper number) and (3) and (4) (number in paranthesis). Comparing the two numbers a good agreement is noticed. This finding gives a good check of the correctness of (9) and (10), which were given by us in order to determine the excited state absorption cross sections σ_{S_1} and σ_{T_1}.

The stimulated emission cross section spectrum, $\sigma_e(\tilde{\nu})$, of anthracene (I) shows a mirror image relationship to the absorption spectrum $\sigma_{S_0}(\tilde{\nu})$ (see Fig. 5a) and a very small Stokes shift of the 0–0 transition. This indicates that the vibrational spacings of the Franck-Condon (FC) and equilibrium (EQ) excited states are similar. As can be seen from Figs. 5b, 6 and 7, the mirror symmetry is partly lost in the above spectra of the substituted derivatives of anthracene. Already substitution of the –OAc group in position 9 of the anthracene ring (Fig. 5b) modifies the intensity of the vibrational peaks, but does not change the frequencies. This holds for compounds III–VI notwithstanding the spectra are more blurred. The phenyl group introduced at position 9 or 10 in the anthracene ring modifies the $\sigma_e(\tilde{\nu})$ spectrum in a somewhat different way (see Figure 7b). The emission spectrum of 2,9-diacetoxy-3-methoxy-9-phenylanthracene shows a very weak vibrational structure. It is diffused in the dioxane solution at room temperature. These findings indicate that the nuclear conformation of the equilibrium excited $S_1(^1B_{2u})$ state is different from that of the ground state $S_0(^1A_{1g})$ and that rotational vibrations of the –Ph, –OAc or –Me groups cause diffusion of the fluorescence spectrum.

The results of our measurements can be summarized as follows:

a) The absorption spectra $S_0(^1A_{1g}) \rightarrow S_1(^1B_{2u})$ of all compounds are shifted to longer wavelengths in comparison to anthracene. The positions of the excited state absorption spectra $S_1(^1B_{2u}) \rightarrow S_n(^1A_{1g})$, $S_1(^1B_{2u}) \rightarrow S_k(^1B_{1g})$ depend little on the kind of substituent and its position. The phenyl group substituted in position 9 is an exception. The values of the absorption cross sections of the $^1B_{2u} \rightarrow {}^1A_{1g}$ band are constant for compounds I, III, VI and VII and about 30% lower for the others.

Table 3. Comparison of the anthracene triplet-triplet absorption cross sections, $\sigma_{T_1}^{\max}(\lambda) \times 10^{-17}$ [cm^2], for various solvents with literature data ($T = 290$ K). [a] This work.

Benzene	Cyclohexane	Alc.ethyl.	Dioxane
– (430.6 nm) [a]	24.0 [a] (423.0 nm)	19.8 [a] (420.7 nm)	25.0 [a] (425.9 nm)
17.5 [18] (432.5 nm)	24.9 [18] (425 nm)	19.2 [20] (419 nm)	
20.4 [21] (428.5 nm)	33.0 [20] (422.5 nm)	28.8 [22] (421 nm)	
16.1 [23] (431 nm)	20.2 [23] (423 nm)	18.6 [23] (421 nm)	

The triplet absorption band $T_1(^3B_{2u}) \rightarrow T_n(^3B_{1g})$ of compounds III–VII is shifted to longer wave lengths in comparison to anthracene. Its intensity decreases from about 40 to 62% for the compounds II–VII, respectively.

c) Good agreement between the σ_{S_1} and σ_{T_1} values calculated using (3), (4) and (9), (10) gives confidence that the theoretical principles of the proposed method for determination of the excited state absorption cross sections is correct. The agreement of our results (obtained for anthracene) with those of other authors [18–23] supports the σ_{S_1} and σ_{T_1} values determined for the compounds under study (see Table 3).

As a conclusion it can be stated that the excited state $^1B_{2u} \rightarrow {}^1A_{1g}$, $^1B_{2u} \rightarrow {}^1B_{1g}$ and $^3B_{2u} \rightarrow {}^3B_{1g}$ absorption measurements give further information about the electronic structure of the compounds; they are supplementary to those obtained from the ground state $^1A_{1g}$, absorption studies. In our measurements we have determined the energy values of excited states which are not attainable from absorption from the ground state. Such measurements performed for dyes give important information about their usefulness as active media in dye lasers.

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