Luminescence and Laser Properties of the 10-Phenyl-9-acetoxyanthracene Derivatives

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Absorption and fluorescence spectra, fluorescence quantum yield and decay time have been measured for eight new 10-phenyl-9-acetoxyanthracene derivatives. It is found that the strength of the absorption transition is independent of the phenyl and anthracene substitution, whereas the strength of the fluorescence transition depends more on the functional groups substituted in the anthracene ring then in the phenyl ring. The loss of mirror symmetry between the absorption and emission spectra and the large values of the Stokes shift suggest that, due to perturbation of the functional groups, the molecular geometries of the S_0 and S_1^* states are different.

The investigated compounds show laser action. The relative value of the absorption threshold power, the gain spectra and the lasing region have been determined. It is found that the amplified spontaneous emission and gain spectra depend on the interaction of the substituted phenyl ring with the π-electrons of the anthracene ring.

Introduction

Anthracene derivatives show bigger luminescence quantum yields (Q_F), the absorption and emission spectra are shifted to longer wavelengths, and often they possess smaller fluorescence mean decay times than unsubstituted anthracene. For this reason some of the molecules are used in scintillators [1] and in dye lasers as active media [2].

In this paper we present the results of luminescence and laser emission studies on nine derivatives of 10-phenyl-9-acetoxyanthracene (I), namely:

10-(4′-acetoxyphenyl)-9-acetoxyanthracene (II),
10-(4′-methylphenyl)-9-acetoxyanthracene (III),
10-(2′-acetoxyphenyl)-9-acetoxyanthracene (IV),
10-(2′,4′-diacetoxyphenyl)-9-acetoxyanthracene (V),
10-(4′-acetoxyphenyl)-2,9-diacetoxyanthracene (VI),
10-(4′-acetoxyphenyl)-2-methyl-9-acetoxyanthracene (VII), 10-phenyl-2-methyl-9-acetoxyanthracene (VIII), and 10-(4′-methylphenyl)-2-methyl-9-acetoxyanthracene (IX).

The absorption and emission spectra in ethanol solution and the laser emission of some of then in dioxane were reported in earlier papers [3, 4].

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1. Luminescence Studies

1.1. Apparatus, materials and procedures

The compounds were recrystallized from ethanol and their purity was checked chromatographically. The concentration in the spectroscopically pure solvent dioxane was 5×10^{-5} mol/l. The absorption spectra were measured with a Zeiss-Jena type VSU spectrophotometer. The emission spectra, excited at 365 nm, were recorded using a Zeiss-Jena SPM-2 grating monochromator.

The quantum yields were measured photoelectrically (Kawski *et al.* [5]). The apparatus was calibrated by mean of a solution of 9,10-diphenylanthracene, for which the fluorescence quantum yield is well known [6]. The quantum yield was calculated from the expression

$$Q_F = Q_F^R \frac{\int_0^\infty I_F(\nu)\,d\nu}{\int_0^\infty I_F^R(\nu)\,d\nu} \cdot \frac{\varepsilon(\nu)}{\varepsilon^R(\nu)} \left(\frac{n}{n^R}\right)^2, \qquad (1)$$

where $I_F(\nu)$, $I_F^R(\nu)$ and $\varepsilon(\nu)$, $\varepsilon^R(\nu)$ are the fluorescence spectra and the molar extinction coefficients of the measured and reference solutions, and n and n^R are the mean refractive indices of the solvents.

The fluorescence decay times were measured with a phase-fluorometer constructed by Bauer *et al.* [7]. As a reference fluorophor, dimethyl POPOP in

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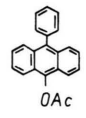
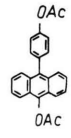
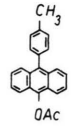
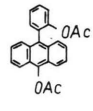
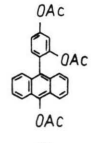
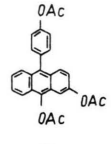
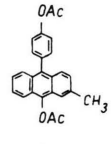
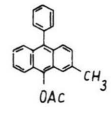
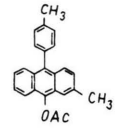
Table 1. Calculated lifetimes τ_A^0; centers of gravity of the absorption ν_A^{cg} and emission ν_F^{cg} spectra and experimentally determined mean decay times τ_{exp}; quantum yields Q_F and widths of the absorption and emission spectra of 10-phenyl-9-acetoxyanthracene derivatives in dioxane.

No.	Molecule	ε_{max} [l mol^{-1} · cm^{-1}] $\int \varepsilon(\nu)\, d\ln\nu$ $\times 10^{-3}$	$\langle \nu^{-3} \rangle_{AV}^{-1}$ $\times 10^{13}$	τ_A^0 / τ_F^0 in ns	τ_{exp} [ns] Q_F	FWRE(A) FWRE (F) Δ in cm^{-1}	ν_A^{cg} / ν_F^{cg} in cm^{-1} $\nu_{ST} = \frac{1}{2}(\nu_A^{cg} - \nu_F^{cg})$
1	2	3	4	5	6	7	8
0		8.600 1.034	1.239	16.58 13.61	4.8 0.36	3 700 3 400 300	28 685 25 224 1 731
I		12.300 1.359	1.253	10.12 9.36	9.07 0.97	3 750 3 600 150	26 971 23 409 1 781
II		11.800 1.314	1.296	10.12 9.26	8.88 0.96	3 900 3 600 300	27.056 23.640 1.708
III		11.500 1.314	1.231	10.60 9.26	8.69 0.94	3 750 3 450 300	27 230 23 650 1 790
IV		11.300 1.248	1.259	10.96 9.93	9.33 0.94	3 850 3 400 450	27 286 23 604 1 841
V		11.800 1.320	1.293	10.09 9.39	9.06 0.97	4 000 3 400 600	27 112 23 610 1 751
VI		10.100 1.326	1.214	10.71 11.26	9.46 0.84	5 150 3 750 1 400	27 206 23 406 1 900
VII		9.600 1.337	1.228	10.49 11.99	9.23 0.77	4 700 3 700 1 000	27 035 23 194 1 920
VIII		9.820 1.294	1.276	10.43 12.24	9.55 0.78	4 800 3 600 1 200	27 104 23 200 1 952
IX		8.600 1.300	1.262	10.50 11.22	9.20 0.82	4 750 3 700 1 050	27 161 23 148 2 007

ethanol, was used in place of the usual scattering reference. The emission wavelengths of the reference fluorophor and the sample were measured by a monochromator, and the relative phase angle $\Delta\varphi$ of the output signals by means of a digital phasemeter. The decay time is calculated as $\tau_{exp} = \text{tang}\, \Delta\varphi/2\pi\nu$, ν being the modulation frequency. In Table 1, column 6, the mean values of four runs are given. The accuracy of the fluorescence decay time and the quantum yield depends on the accuracy of the determination of τ and Q_F for the reference fluorophore. We estimate the errors of τ_{exp} and Q_F to be: ± 0.1 ns and ± 0.05, respectively.

The absorption and fluorescence spectra are shown in Figs. 1a and 1b. The values of the molar extinction coefficient ε_{max} of the anthracene ring-localized mode and the integral $\int \varepsilon(\nu)\, d\ln\nu$ are given in Table 1, column 3. The fluorescence spectra are normalized to the maximum value. All measurements were carried out at room temperature.

Correlations between the nuclear topology of the molecules and their spectroscopic properties as to the most important quantities involving the long wave electronic transition have been found. First of all the lifetime of the S_1^* state has been calculated using the formula of Strickler and Berg [8]:

$$\tau_A^0 = 2.88 \cdot 10^{-9} n^2 \frac{\int I_F(\nu)\, d\nu}{\int \nu^{-3} I_F(\nu)\, d\nu} \cdot \int \varepsilon(\nu)\, d\ln\nu . \qquad (2)$$

The τ_A^0 value can be compared with the natural radiative lifetime

$$\tau_F^0 = \tau_{exp} \cdot Q_F^{-1} \qquad (3)$$

determined using the fluorescence decay time τ_{exp} and the quantum yield Q_F measured in this experiment. $1/\tau_A^0$ and $1/\tau_F^0$ reflects the strength of the absorption and fluorescence transition, respectively.

The energy difference between the centers of gravity of the long wave absorption and ν_A^{cg} and emission spectrum ν_F^{cg} gives the Stokes shift:

$$\nu_{ST} = (\nu_A^{cg} - \nu_F^{cg})/2 . \qquad (4)$$

The frequencies of the center of gravity of the absorption and fluorescence spectra are defined as

$$\nu_A^{cg} = \int \nu\, \varepsilon(\nu)\, d\nu / \int \varepsilon(\nu)\, d\nu ,$$
$$\nu_F^{cg} = \int \nu\, I_F(\nu)\, d\nu / \int I_F(\nu)\, d\nu . \qquad (5)$$

The integrals appearing in [2] and [5] are determined from our measurements using the method of

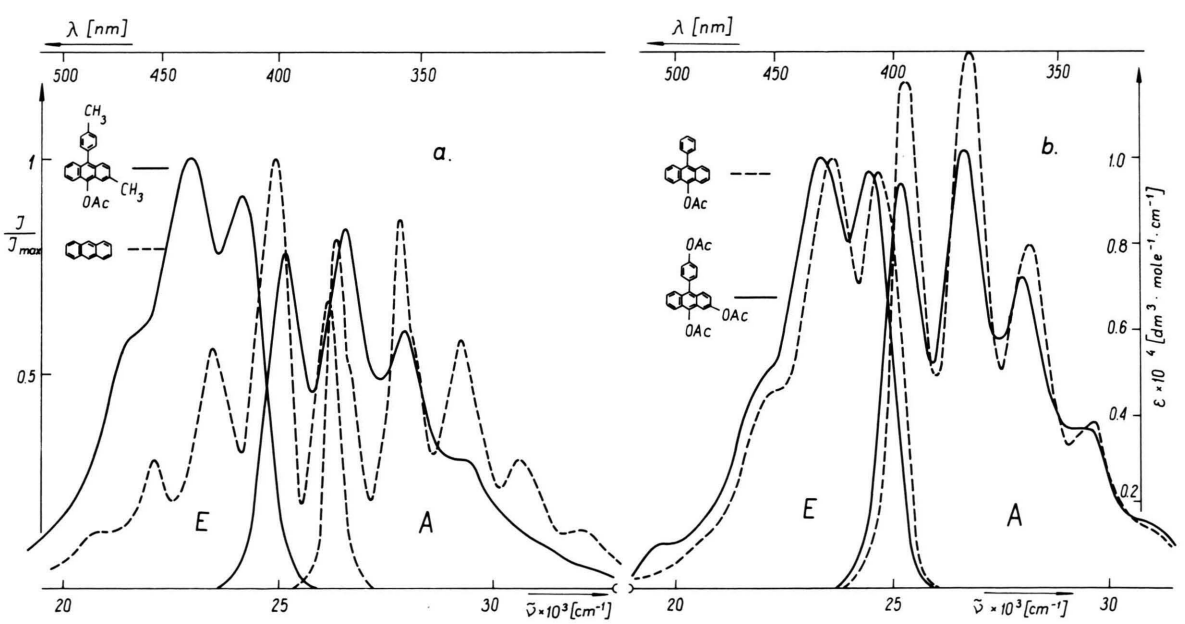


Fig. 1. Absorption and fluorescence spectra of: a) anthracene (---), 10-(4′-methylphenyl)-2-methyl-9-acetoxyanthracene (——); b) 10-phenyl-9-acetoxyanthracene (---); 10-(4′-acetoxyphenyl)-2,9-acetoxyanthracene (——) in dioxane.

Simpson [9]. The computed values of τ_A^0 and τ_F^0 are collected in Table 1 column 5, the values of ν_A^{cg}, ν_F^{cg} and frequencies of Stokes shift ν_{ST} in column 8.

As shown by Berlman [10], the band widths of the absorption and fluorescence spectra are useful quantities in conformation studies of a chromophore in its ground and first excited singlet state of a series of related compounds. In Table 1, column 7, are given the widths (in cm^{-1}) of the absorption and fluorescence spectra (at height of 37% of the maximum value of $\varepsilon(\nu)$ and $I_F(\nu)$). Columns 3 and 4 give the pertinent data used in calculating the natural radiative lifetime. The maximum extinction coefficient of the first band for each compound is given also in Table 1, column 3. In calculating the natural radiative lifetime, we used in [2] the refractive index of the pure solvents; for dioxane it is equal to 1.42.

1.2. Discussion of the spectroscopic properties

The investigated compounds can be separated into two groups considering the substitution of the acetoxy $-OCOCH_3$ (−OAc) or the methyl $-CH_3$ (−Me) groups in the 10-phenyl-9-acetoxyanthracene molecule. In the first group (compounds I−V) one or two of the hydrogen atoms on the phenyl ring are replaced by acetoxy or methyl groups. In the second group the above groups are introduced additionally at position 2 in the anthracene ring.

The bathochronic effect of those derivatives was discussed in detail in our earlier work [3]. Our present and earlier measurements [3] show that the spectra of both groups are modified in a somewhat different way. The difference shows up in a blurred vibrational structure, in a loss of mirror symmetry and in different extinction coefficients of the $^1A \rightarrow {}^1L_a$ band. The results can be summarized as follows:

a) The extinction coefficients, ε_{max} (see Table 1, column 3) of the first group of compounds are larger than those for molecules of the second group. The difference amounts to about 20%. Both groups have larger values of $\varepsilon(\nu)$ than the unsubstituted anthracene disolved in dioxane ($\varepsilon_{max} = 8600$). But the values of the absorption integral $\int \varepsilon(\nu)\, d\ln\nu$ are nearly equal for both groups.

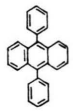
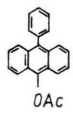
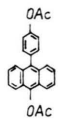
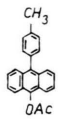
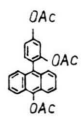
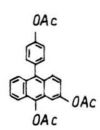
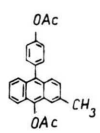
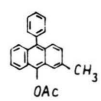
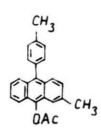
b) Compounds with a short fluorescence decay time have a large quantum yield, and *vice versa*. This rule is very useful in nuclear conformation studies of the ground and first excited singlet state. The ratio of the rate constants $k_F/(k_{IC} + k_{ISC})$ differs by one order of magnitude for the two groups of compounds (see Table 2, column 3), being smaller for the second group. The values of Q_F and τ_{exp} for the derivatives of 10-phenyl-9-acetoxyanthracene are bigger than for the unsubstituted anthracene molecule.

c) the τ_F^0 values of the compounds of the two groups differ by about 2.2 ns in the average, being smaller than that of anthracene ($\tau_F^0 = 13.6$ ns) in both groups. The lifetime τ_A^0, calculated from the absorption and emission spectra, has nearly the same value for all compounds. The differences between particular molecules are within the error range of the integrals in (2). The reciprocal of the mean value of $\langle \nu^{-3} \rangle_{AV}$ in the fluorescence spectrum has practically the same value for each molecule (see Table 1, column 4). The average value of τ_A^0 (10.45 ± 0.3 ns) is larger than τ_F^0 for the first and smaller for the second group of compounds.

Taking these findings into account, as well as the fact that the absorption spectra show obviously a similar shape, it can be concluded that all these compounds possess the same strength of the first absorption transition. This indicates that the functional groups do not influence explicitly the π-electrons of the anthracene ring in the ground state. This is in agreement with results of Berlmann [10] and Jones [11] obtained for phenyl- and diphenylanthracene.

It has been shown by many authors [10−14] that electronic excitation changes the electron density distribution in the molecule, which often causes substantial alteration of the molecular geometry and the solvent cage in the excited state. Therefore a comparison of the absorption and emission spectra gives information concerning the relative geometries and solvatation sphere of the ground and first excited singlet states. The differences in the S_0 and S_1^* geometries are reflected in the mirror symmetry of the spectra and in the Stokes shift. The mirror symmetry is not strictly preserved in our molecules. Discrepancies are more evident for the second group of compounds; corresponding differences can be seen between FWRE (A) and FWRE (F) also (see Δ in Table 1, column 7). The Δ-value amounts to 200 and 700 cm^{-1} for the two groups, respectively. The Stokes shift (see column 8) for molecules of the second group has by about 200 cm^{-1} larger

Table 2. Calculated fluorescence rate constants, k_F; sums of the rate constants of intra and intersystem crossing, $k_{IC} + k_{ISC}$; induced emission cross sections, σ_{em}; relative thresholds; gain values, $G(\lambda)$; and lasing regions of 10-phenyl-9-acetoxyanthracene derivatives in dioxane.

No.	Compounds	$k_F = Q_F \cdot \tau_{exp}^{-1}$ [s^{-1}] $k_{IC} + k_{ISC}$ [s^{-1}]	$\sigma_{max}^{em} \times 10^{-17}$ [cm^2]	Threshold (rel. value)	Gain values [cm^{-1}]	Lasing region [nm]
1	2	3	4	5	6	7
0		$12.9 \cdot 10^7$ $1.2 \cdot 10^6$	4.90	1.00	$5.51_{\lambda=433}$	425.9–445.2
I		$10.7 \cdot 10^7$ $3.3 \cdot 10^6$	4.30	1.41	$3.59_{\lambda=430}$	419.8–430.4
II		$10.8 \cdot 10^7$ $4.5 \cdot 10^6$	4.12	1.43	$3.29_{\lambda=429}$	425.4–436.4
III		$10.8 \cdot 10^7$ $6.9 \cdot 10^6$	4.45			
IV		$10.1 \cdot 10^7$ $6.4 \cdot 10^6$	3.96	1.22	$3.52_{\lambda=426}$ $1.74_{\lambda=450}$	420.9–431.6 446.8–453.5
V		$10.7 \cdot 10^7$ $3.3 \cdot 10^6$	4.31	1.28	$3.18_{\lambda=427}$ $1.327_{\lambda=450}$	421.7–433.5 446.4–456.9
VI		$8.9 \cdot 10^7$ $17.1 \cdot 10^6$	3.43	1.79	$2.65_{\lambda=435}$	423.2–434.0
VII		$8.3 \cdot 10^7$ $25.2 \cdot 10^6$	3.41	1.54	$3.45_{\lambda=433.5}$	427.5–439.9
VIII		$8.2 \cdot 10^7$ $23.0 \cdot 10^6$	3.27	1.52	$3.13_{\lambda=430}$	428.3–437.4
IX		$8.9 \cdot 10^7$ $19.0 \cdot 10^6$	3.48	1.43	$3.64_{\lambda=435}$	429.3–441.3

values. The differences of the Stokes shifts are beyond the error range of ν_A^{cg} and ν_F^{cg} found from (5). These findings are in agreement with the earlier statements concerning the k_F, τ_A^0 and τ_F^0 values. They indicate a difference of molecular geometry of the two groups of molecules in the ground, S_0, and first excited singlet state, S_1^*.

The spectroscopic evidence may be summarized in three points:

1. The strength of the absorption transition, $1/\tau_A^0$, is independent of the group $-$OAc and $-$Me substituted in the phenyl ring as well as in the position 2 of the anthracene ring.

2. For the series of related compounds the strength of the fluorescence transition, $1/\tau_F^0$, depends more on the groups substituted in the anthracene ring than in the phenyl ring.

3. The structured absorption spectrum, the diffuse fluorescence spectrum, the loss of mirror symmetry, the large Stokes shift and the rather large ε_{max} value suggest, according to Berlman [10], that for the molecules under study the perturbed anthracene ring has different configurations in the S_0 and S_1^* states. This effect is greater for the molecules of the second group.

2. Laser Emission Studies

The intensity of the amplified spontaneous emission as well as the spectrum of the laser light depends on various molecular coefficients. The most important are the absorption and emission cross sections. The latter one depends on the quantum yield and mean decay time of the fluorescence. For many compounds the appearance of induced emission depends on the cross sections of the $S_1^* \rightarrow S_n^*$ and $T_1 \rightarrow T_n^*$ transitions. For most dyes the rate constants of the above transitions are unknown. The population densities of the S_1^* and T_1 levels can give some information concerning the $S_1^* \rightarrow S_2^*$ and $T_1 \rightarrow T_n^*$ transitions. The population densities of the S_1^* and T_1 states depend on the pump power and on the rate constant of the intersystem crossing, k_{ISC}. The maximum value of k_{ISC} can be calculated from the formula

$$k_{ISC} \leqq k_{IC} + k_{ISC} = k_F (1 - Q_F) Q_F^{-1}, \qquad (6)$$

where $k_F = Q_F/\tau_{exp}$ and k_{IC} is the rate constant for internal conversion. The calculated values of the fluorescence rate constant k_F, and the sum of $k_{IC} + k_{ISC}$ are given in Table 2, column 3. Whereas diphenylanthracene has a fluorescence rate constant about 20% higher than the compounds of the first group and 40% higher than the compounds of the second group, the sum $k_{IC} + k_{ISC}$ is smaller than the value for both groups of molecules; for the second group by about one order of magnitude. These data and the values of the cross sections $\sigma_{S_0}(\lambda)$, $\sigma_{em}(\lambda)$/ (see Fig. 2 and Table 2, column 4) give information about possible laser action.

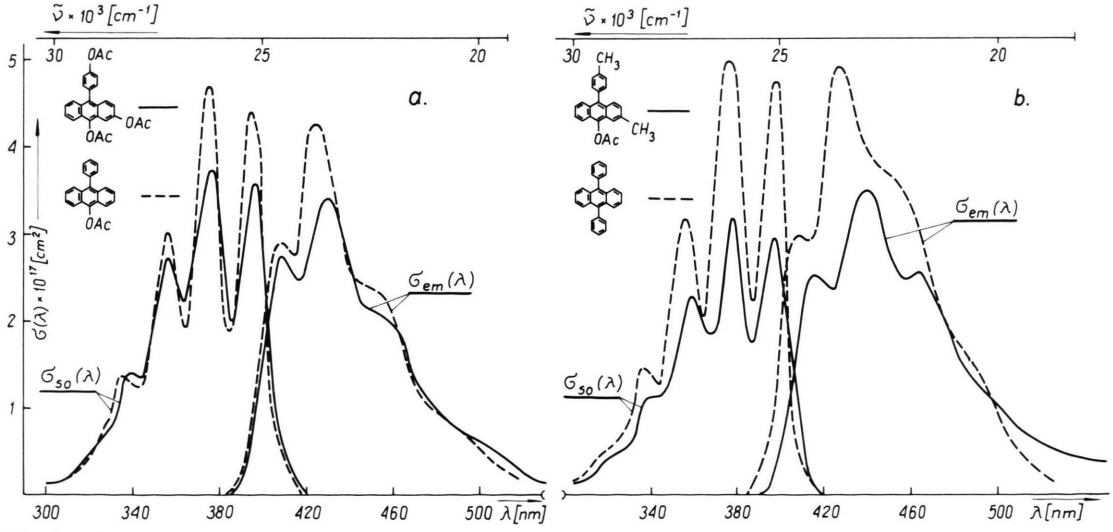


Fig. 2. Absorption and emission cross sections of: a) 10-(4′-acetoxyphenyl)-9-acetoxyanthracene (——); 10-phenyl-9-acetoxyanthracene (- - -); b) 10-(4′-methylphenyl)-2-methyl-9-acetoxyanthracene (——); 9,10-diphenylanthracene (- - -) in dioxane.

From the cross section spectra (Fig. 2) and from column 3 and 4 of Table 2 it is obvious that the derivatives of 10-phenyl-9-acetoxyanthracene may not be so useful as active media of a dye laser. That can be seen by the gain spectra, the threshold pump power and the spectral tuning range determined and compared with the data for diphenylanthracene.

2.1. Threshold determination and gain spectra

To measure the gain spectra an arrangement with a selfbuilt N_2-laser, a dye cell, a monochromator and a light detecting system, as described earlier [4], was used. The gain cell was transversally pumped, using cylindrical focusing optics giving a variable active length. At constant N_2-light power it was easy to determine the critical active length l_{Th} to obtain amplified emission. The product $l_{Th} \cdot \varepsilon(\lambda)$ (at $\lambda = 337.1$ nm) has been assumed to be proportional to the threshold of absorbed power. The values relativ to the value of diphenylanthracene are given in Table 2, column 5.

As it was shown in the paper of Broida *et al.* [13], for this class of compounds it is easy to observe saturation effects. In order to control the influence of saturation on the gain factor $G(\lambda)$ we checked the validity of the law $J_{ASE} \propto \exp[G(\lambda) \cdot l]$. For some compounds the threshold length l_{Th} was bigger than 1 cm and saturation was obtained changing the active length by a few mm. Here we calculated $G(\lambda)$ using the improved formula obtained on the basis given by Shank *et al.* [12]:

$$G(\lambda) = \frac{3}{l} \ln \left[\frac{J_l}{2J_{2l/3}} - \frac{1}{2} + \frac{1}{2} \left(\left(\frac{J_l}{J_{2l/3}} \right)^2 + \frac{2J_l}{J_{2l/3}} - 3 \right)^{1/2} \right], \tag{7}$$

where J_l and $J_{2l/3}$ are the amplified emission intensity of the full and 2/3 cell length, respectively. Defining (l_{Th}) the full pump region ($l = 3/2\, l_{Th}$) was determined for each compound.

Figures 3a, 3b and 3c show the amplified emission spectra obtained for pump regions 0.66 and 1.00 cm (solid lines) and the calculated gain spectrum (heavy dashed line). The above spectra of the remaining compounds are similar in shape to those in Figs. 3a, 3c (compounds no. 0, II, III, VI, VII,

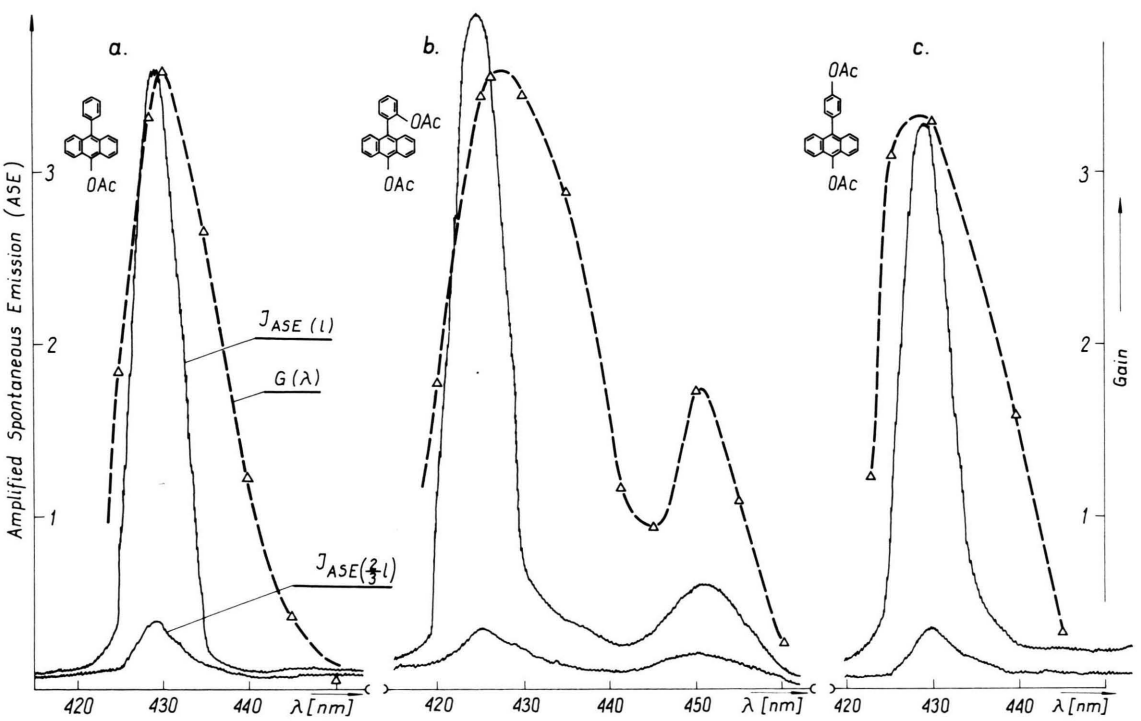


Fig. 3. Amplified spontaneous emission spectra of: a) 10-phenyl-9-acetoxyanthracene; b) 10-(2′-acetoxyphenyl)-9-acetoxyanthracene; c) 10-(4′-acetoxyphenyl)-9-acetoxyanthracene in dioxane solution. The computed gain spectra are drawn with heavy dashed line.

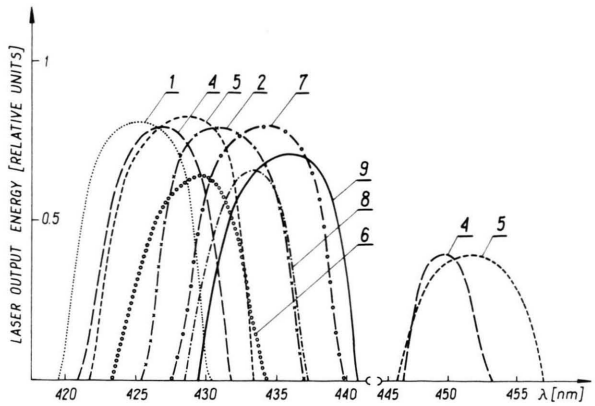


Fig. 4. Laser output energy curves of 10-phenyl-9-acetoxyanthracene derivatives in dioxane relative to diphenylanthracene. The curves are numbered like the compounds in Table 1 and 2.

VIII and IX) or Fig. 3b (compounds no. I, IV and V). It must be pointed out that only the compounds with a functional group substituted in the position 2′ of the phenyl ring show two distinct peaks in the ASE and gain spectra. The peak distance is equal to the $\Delta\nu$ value of the ring-localized vibrational modes in the fluorescence spectrum. The peak values $G_{max}^{(\lambda)}$ are given in Table 2, column 6.

2.2. Determination of the lasing region

The lasing region was determined by means of a simple Hänsch type dye laser set-up. The laser wavelength was changed with a Bausch & Lamb grating (1800 grooves/mm), mounted on a rotative micrometer screw-holder, and determined photoelectrically using a Zeiss grating monochromator. The lasing region is given in Table 2, column 7 and in Figure 4. Laser light can be obtained with good efficiency in the region 420–440 and 445–458 nm using three dyes, *i.e.* 10-phenyl-9-acetoxyanthracene; 10-(4′,2′-acetoxyphenyl)-9-acetoxyanthracene and 10-phenyl-2-methyl-9-acetoxyanthracene. The compounds of the second group have an about 15% smaller output energy than the compounds of the first group. In Fig. 4 the laser output energy is given in units of output energy of diphenylanthracene. The width of the output energy curve depends for the second peak on the number and kind of the functional groups in the phenyl ring. This dependence will be comprehensively discussed elsewhere [15].

The laser emission studies of the 10-phenyl-9-acetoxyanthracene derivatives can be summarized as follows:

1. Our derivatives of 10-phenyl-9-acetoxyanthracene lase at room temperature in some organic solvents (dioxane, benzene, cyclohexane, toluene), where the quantum yield is higher then 0.8.

2. The compounds do not show bleaching effects, but the fairly long decay time of the triplet state ($\tau_T \sim 10^{-7}$ s), demands a pumping or mixing device in the dye laser arrangement.

3. The appearance of a second peak in the output energy curve as well as in the ASE and gain spectra can be explained by additional interaction of the –OAc group (in position 2′) with the π-electrons of the anthracene ring. This interaction causes different shifts of the S_1^* and T^* levels [16].

4. The gain and the amplified spontaneous emission spectra of our compounds give some information about the shifts and position of the T_2^* state and its vibration peaks.

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[1] J. B. Birks, Liczniki scyntylacyjne (Polish translation) PWN, Warszawa 1956. A. S. Cherkasov, V. A. Molchanov, T. M. Vember, and K. G. Voldaikina, Dokl. Akad. Nauk. SSSR **109,** 292 (1956).
[2] J. A. Myers, I. Itzkan, and E. Kierstead, Nature London **225,** 544 (1970). J. A. Myer, C. L. Johnson, E. Kierstead, R. D. Sharma, and I. Itzkan, Appl. Phys. Lett. **16,** 3 (1970).
[3] J. Gronowska, K. Aleksandrzak, and J. R. Heldt, Polish J. Chem. **55,** 57 (1981). J. R. Heldt, J. Heldt, and J. Gronowska, Z. Naturforsch. **30a,** 612 (1975). J. Gronowska and J. R. Heldt, Roczniki Chemii **51,** 681 (1977).
[4] J. R. Heldt and J. Heldt, Acta Phys. Polon. **A55,** 79 (1979). J. R. Heldt, J. Szczepanski, and J. Heldt, Optics Comm. **39,** 325 (1981).
[5] A. Kawski, J. Kaminski, and E. Kuten, J. Phys. B. Mol. Phys. **4,** 609 (1971). D. Gloyna, I. Gryczynski, and A. Kawski, Z. Naturforsch. **36a,** 626 (1981).
[6] J. B. Birks, J. Res. NBS, Phys. Chem. **80A,** 389 (1976).
[7] R. K. Bauer and A. Balter, Optics Comm. **28,** 91 (1979).
[8] S. J. Strickler and R. A. Berg, J. Chem. Phys. **37,** 814 (1962).
[9] H. Margenau and G. M. Murphy – The Mathematics of Physics and Chemistry, D. van Nostrand, Copyright 1956, p. 499.
[10] I. B. Berlman, J. Phys. Chem. **74,** 3085 (1970).
[11] R. N. Jones, Chem. Rev. **41,** 353 (1947).
[12] C. V. Shank, A. Dienes, and W. T. Silvfast, Appl. Phys. Lett. **17,** 307 (1970).
[13] H. P. Broida and S. C. Haydon, Appl. Phys. Lett. **16,** 142 (1970).
[14] T. C. Werner, Use of fluorescence to study structural changes and solvatation phenomena in electronically excited molecules, E. L. Wehry, Modern fluorescence spectroscopy, Heyden, Plenum Press, New York 1976.
[15] J. R. Heldt, J. Szczepanski, and J. Heldt, J. Appl. Phys. (in press).
[16] R. S. Becker, Theory and Interpretation of Fluorescence and Phosphorescence, Chapt. II, John Wiley, New York 1969.