Ground- and Excited-State Absorption Spectra of 9-Acetoxy-10(4′-Acetoxy)phenylanthracenes

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The ground- (S_0) and excited- (S_1 and T_1) state spectra of seven derivatives of 9-acetoxy-10(4′-acetoxy)phenylanthracene were determined in the region 50000 – 15000 cm^{-1} (200 – 660 nm). Comparison of these spectra to the unsubstituted molecule (anthracene) indicates the presence of bathochromic shift and the steric effect. The substituents cause changes of positions of the energy levels (bigger shifts are noticed for low lying states) and also changes of the absorption intensities of some transitions. The steric hindrances between the phenyl-substituents and the anthracene skeleton are more pronounced if the –OAc(–Me) group or a heavy atom is introduced at position 2′ of the phenyl ring. Molecules possessing such substituents at the meso-position exhibit spectroscopic properties characteristic for a plane molecule in the S_0 and S_1 states; they show a better preservation of the mirror symmetry between the absorption and fluorescence spectra, lower Stokes shifts and the destabilization energies and bigger fluorescence quantum yields.

1. Introduction

Anthracene has three positions (1, 2 and 9) for monosubstitution, in which the density of the ring electrons differs significantly. The meso-position 9 is the most electron-rich one of the ring, and the bond lies in the direction of the lowest energy transition moment ($S_0(^1A_{1g}) \rightarrow S_1(^1B_{2u})$). It is known from earlier studies [1 – 3] that a complete coplanarity between a substituent at position 9 and the ring is often sterically hindered by the hydrogens at the positions 1 and 8. For substitution in position 2 (which is the least electron-rich position), the substituent axis is more aligned with the direction of the second anthracene transition ($S_0(^1A_{1g}) \rightarrow S_2(^1B_{3u})$) and steric hindrance to coplanarity is almost insignificant. The electron density at position 1 is intermediate between the other two. A group substituted at position 1 lies nearly along the axis of the $S_0(^1A_{1g}) \rightarrow S_1(^1B_{2u})$ transition and the steric hindrance from the ring hydrogens is intermediate compared to positions 2 and 9. The spectral properties of the substituted anthracenes are dependent on the position and on the kind of the functional group.

In our previous studies the spectral properties of mono- and multi-substituted anthracenes were discussed in some detail [4 – 7]. Some of these compounds show lasing [8, 9]. Among the lasing compounds we found a group of molecules with distinctly different laser parameters from the remaining ones. The compounds of this group have an acetoxy and an aryl group (with substituents –OAc, –Me, –F, –Cl, in the position 2′ of the phenyl ring) substituted in the positions 9 and 10 of the anthracene ring, respectively. In the papers [6, 9] it was suggested that the steric hindrance of those substituents by hydrogens of the anthracene ring change the planarity of the molecule during the absorption process.

This paper confirms some earlier suggestions and shows how the different aryl substituents influence the ground state ($S_0 \rightarrow S_1$) and excited state ($S_1 \rightarrow S_k$ and $T_1 \rightarrow T_m$) absorption spectra. The so-called mirror symmetry relation between suitably normalized absorption and emission spectra is given and discussed.

2. Experimental

The structural formulae of the compounds under investigation are given in Table 1. Their synthesis is described in [10]. The purity of these compounds

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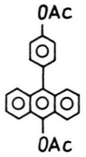
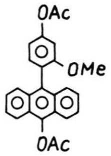
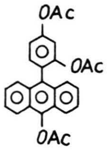
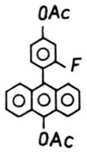
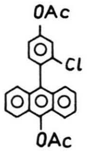
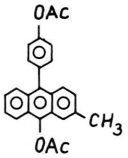
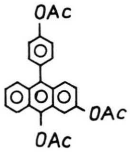
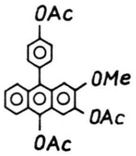
Table 1. The relative intensities of the vibrational peaks, the destabilization energy values and Stokes shifts of 9-acetoxy-10(4′-acetoxy)phenylanthracene derivatives in dioxane.

Compound		Frequencies and intensities of vibrational peaks				Destabilization energy [10^{-2} eV] $\tilde{\nu}_{St} = \tilde{\nu}_0 - \tilde{\nu}_F^{eg}$ [cm^{-1}] and ΔS^2 [%]
		Absorption		Emission		
		$\tilde{\nu}_A$ [cm^{-1}]	$S^2_{GO,Ev'}$	$\tilde{\nu}_F$ [cm^{-1}]	$S^2_{EO,Gv''}$	
I		25 500	0.34 (0.32)	24 800	0.24 (0.28)	8.68 (2.36)
		26 850	0.34 (0.32)	23 550	0.36 (0.34)	
		28 300	0.20 (0.22)	22 200	0.25 (0.24)	1710
		29 750	0.09 (0.10)	20 750	0.11 (0.10)	
		31 200	0.03 (0.04)	19 500	0.04 (0.04)	20 (18)
II		25 500	0.33	25 150	0.25	3.41
		26 900	0.32	23 750	0.36	
		28 300	0.24	22 400	0.25	1530
		29 700	0.08	21 100	0.10	
		31 100	0.03	19 500	0.04	16
III		25 500	0.33	25 150	0.24	5.20
		26 900	0.32	23 750	0.36	
		28 300	0.24	22 400	0.25	1400
		29 700	0.08	21 100	0.11	
		31 100	0.03	19 500	0.04	15
IV		25 500	0.34	25 050	0.26	5.20
		26 900	0.34	23 800	0.35	
		28 350	0.21	22 400	0.26	1530
		29 750	0.09	21 100	0.11	
		31 200	0.02	19 400	0.02	16
V		25 500	0.34	25 150	0.26	4.34
		26 900	0.34	23 900	0.37	
		28 350	0.21	22 500	0.24	1520
		29 750	0.09	21 150	0.11	
		31 200	0.03	19 500	0.02	17
VI		25 400	0.33	24 650	0.25	9.30
		26 750	0.33	23 300	0.40	
		28 150	0.22	21 900	0.20	1660
		29 700	0.09	20 400	0.12	
		31 000	0.03	19 150	0.03	20
VII		25 300	0.33	24 600	0.23	8.68
		26 750	0.33	23 300	0.38	
		28 100	0.21	21 800	0.23	1750
		29 750	0.09	20 350	0.11	
		31 000	0.04	18 900	0.05	20
VIII		25 100	0.29	24 450	0.25	8.06
		26 600	0.28	23 100	0.39	
		27 900	0.24	21 500	0.23	2050
		29 450	0.13	20 100	0.10	
		30 900	0.06	18 500	0.03	22

was of p.a. order. Anthracene (p.a.) was additionally purified by zone melting. The solvents n-heptan and dioxane were of spectral purity.

The ground state absorption spectra in n-heptane $5 \cdot 10^{-5}$ Mol/l were measured with a Perkin-Elmer (model 402) spectrophotometer.

The fluorescence spectra were obtained by means of a photoelectric method described in [11]. The spectral halfwidths of the exciting and fluorescence beams are 6 and 3 nm, respectively. The influence of reabsorption was experimentally minimized, and the spectra were corrected for the response function of the photomultiplier and monochromator.

The excited state absorption measurements of dioxane solutions ($c = 3 \cdot 10^{-3}$ Mol/l) were performed with a laser spectrophotometer described in [7]. It consists of an N_2-dye laser combination having a variable delay (0 – 45 ns) between the exciting (N_2) and the probing (dye) beam. In order to determine the absorbances of the $S_1 \rightarrow S_k$ and $T_1 \rightarrow T_n$ transitions the intensity of the probing beam was measured with and without excitation by the light of the N_2-laser.

For these cases, in accordance with the Lambert-Beer law, the light intensities of the probing beam passing a volume $l \times \delta \times d$ of the sample cell are

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

and

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

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, t_0 is the time delay between the exciting and analysing pulses of the N_2- and dye lasers, τ the half width of the dye laser pulse and d the absorption depth for which $\sigma_{S_0}(337.1)\ N_{S_0}\, d = 1$. I_0 is the light intensity of the entrance beam of the dye laser. Taking into account that the decay time $\tau_{S_1} \ll \tau_{T_1}$, we are able to find such a delay between the exciting and analysing laser pulses that in the solution one finds excited molecules in the S_1 or T_1 state only [7]. Then the absorbances at a particular wavelength of the $S_1 \rightarrow S_k$ or $T_1 \rightarrow T_n$ transition are given by formulae

$$A_{S_1}(\tilde{\nu}) = \frac{1}{2.303} \cdot \ln\left(\frac{I_t^0(\tilde{\nu})}{I_t(\tilde{\nu})}\right)_{t_0 = 2\ \mathrm{ns}} = \frac{\sigma_{S_1}(\tilde{\nu}) \cdot l}{2.303} \cdot \bar{N}_{S_1}, \tag{3}$$

$$A_{T_1}(\tilde{\nu}) = \frac{1}{2.303} \cdot \ln\left(\frac{I_t^0(\tilde{\nu})}{I_t(\tilde{\nu})}\right)_{t_0 = 40\ \mathrm{ns}} = \frac{\sigma_{T_1}(\tilde{\nu}) \cdot l}{2.303} \cdot N_{T_1}^{\max}, \tag{4}$$

where $\bar{N}_{S_1}$ and $N_{T_1}^{\max}$ are the average numbers of molecules in te S_1 and T_1 states, respectively (taken over the whole pumping volume of the N_2-laser, only). The unknown values $\bar{N}_{S_1}$ and $N_{T_1}^{\max}$ can be eliminated by comparison [7], performing identical measurements for a compound whose $\sigma_{S_1}(\tilde{\nu})$ and $\sigma_{T_1}(\tilde{\nu})$ spectra are known.

Labelling by s and x the proper constants of the reference and unknown compounds, respectively, the absorption cross sections $\sigma_{S_1}(\tilde{\nu})$ and $\sigma_{T_1}(\tilde{\nu})$ can be determined using the formulae [7]

$$\sigma_{S_1}^{x}(\tilde{\nu}) = \sigma_{S_1}^{s}(\tilde{\nu})\, \frac{A_{S_1}^{x}(\tilde{\nu})}{A_{S_1}^{s}(\tilde{\nu})} \cdot \frac{[1 - \exp(-\sigma_{S_0}^{s}(337.1) \cdot N_{S_0}^{s} \cdot D)]}{[1 - \exp(-\sigma_{S_0}^{x}(337.1) \cdot N_{S_0}^{x} \cdot D)]}, \tag{5}$$

$$\sigma_{T_1}^{x}(\tilde{\nu}) = \sigma_{S_1}^{s}(\tilde{\nu})\, \frac{A_{T_1}^{x}}{A_{T_1}^{s}} \cdot \frac{1 - Q_F^{s}}{1 - Q_F^{x}} \cdot \frac{[1 - \exp(-\sigma_{S_0}^{s}(337.1) \cdot N_{S_0}^{s} \cdot D)]}{[1 - \exp(-\sigma_{S_0}^{x}(337.1) \cdot N_{S_0}^{x} \cdot D)]} \tag{6}$$

without knowledge of the density of molecules in the S_1 and T_1 states. In Eq. (6) the probing beam diameter $D = 0.15$ cm. Anthracene was used as standard.

3. Results and Discussion

3.1. *The mirror and symmetry relationship*

The structural changes in the ground- and excited state geometries of a molecule and its solvent cage can be determined by the degree of mirror symmetry of the corresponding absorption and fluorescence spectra. As it was shown by Blochincev [12], Förster [13 and Stepanov [14], the mirror image similarity is noticed only if the following conditions are fulfilled:

a) the transition moments for the absorption and emission processes are equal, i.e. $Q_{\mathrm{GO,\,Ev'}}(R) \simeq Q_{\mathrm{EO,\,Gv''}}(R)$;

b) the population densities of the vibrational levels of the ground and excited states at unit energy intervals $\Delta\varepsilon''$ and $\Delta\varepsilon'$ weighted by the statistical population factor $g_G(\varepsilon'')$ and $g_E(\varepsilon')$, are equal;

c) the following relations between the frequencies of the absorption and emission spectra are valid:

$$2\,\tilde{\nu}_{0,0} - \tilde{\nu}_{ED,Gv''} \simeq \tilde{\nu}_{GO,Ev'}, \quad \tilde{\nu}_{EO,GO} \simeq \tilde{\nu}_{GO,EO} \simeq \tilde{\nu}_{0,0}.$$

In order to analyze the mirror symmetry we have normalized the absorption and fluorescence spectra in a way suggested by Stepanov [14]. Figure 1 shows the spectra of the three compounds studied as an example (anthracene is given for comparison). Their analysis reveals a distinct similarity in the absorption spectra. The emission spectra show a blurring of the vibration structure and the relative intensity distribution of the vibrational peaks is different from that in the absorption spectrum and from the anthracene emission. By decomposing the spectra in the way shown in Fig. 1b, the relative values of the Franck-Condon factors and the wave numbers of the separated vibrational transistions can be determined. By an analysing these data (see Table 1) we find that (neglecting the batochromic effect which will be discussed later) the wave number differences between neighbouring vibrational peaks ($\tilde{\nu}_{GO,Ev'} - \tilde{\nu}_{GO,Ev'+1}$ and $\tilde{\nu}_{EO,Gv''} - \tilde{\nu}_{EO,Gv'+1}$) in the absorption and emission spectra differ from those of anthracene. The vibrational spacings in the emission are generally smaller than in the absorption. The peak intensities in the absorption spectra equal the corresponding ones of anthracene (see Table 1, column 3).

In the fluorescence spectra the distribution differs from that of anthracene. Especially it is evident for the vibrational transition $v' = 0 \rightarrow v'' = 0$ and 3

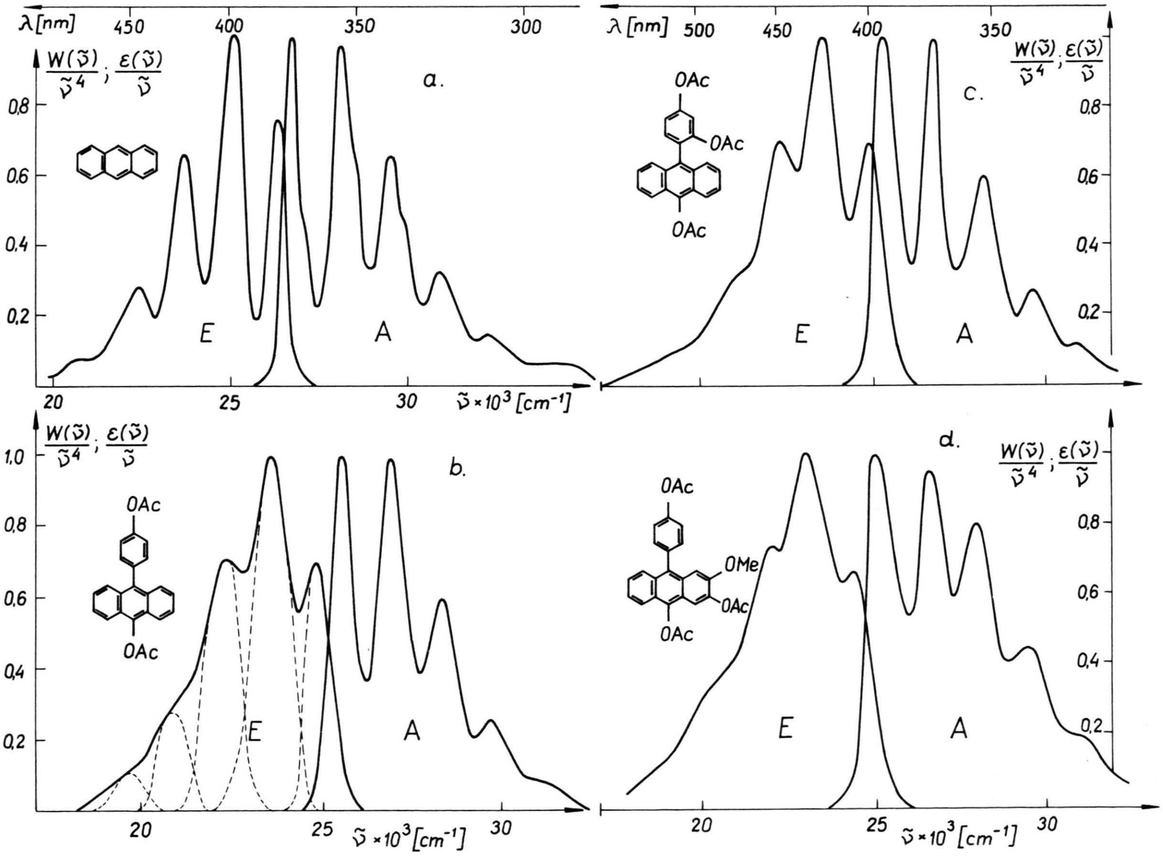


Fig. 1. Normalized absorption (A) and emission (E) spectra of some anthracene derivatives in n-heptane.

where the difference between the Franck-Condon factors is $|S^2_{\mathrm{EO,GO}} - S^2_{\mathrm{GO,EO}}| \simeq 0.1$. For the other vibrational transition the above value is about 0.05. The observed changes of the spectral structure can be explained using a four energy level diagram (see Figure 2). The absorbing and emitting states are classified as thermal equilibrium (EQ) ground and excited states. The molecules from the Franck-Condon states (FC) rearrange the nuclear configuration characterized by the Franck-Condon destabilization energies ΔE_{S_1} and ΔE_0. It follows from Fig. 2 that

$$\Delta E_{\mathrm{S}_1} + \Delta E_{\mathrm{S}_0} \simeq h\,c\,(\tilde{\nu}^{\mathrm{A}}_{0.0} - \tilde{\nu}^{\mathrm{E}}_{0.0}). \tag{8}$$

The destabilization energy of the compounds under study are collected in column 6 of Table 1 (upper numbers). In the same column (lower numbers) the values of the Stokes shift and the departure from the mirror symmetry reationship definite as

$$\tilde{\nu}_{\mathrm{St}} = \tilde{\nu}_{0,0} - \tilde{\nu}^{\mathrm{F}}_{cg} \; [15]$$

and

$$\Delta S^2 = \sum_{v'\,v''} |S^2_{\mathrm{EO,G}v''} - S^2_{\mathrm{GO,E}v'}|^2 \cdot 100\%,$$

respectively, are given.

The compounds can be divided into two groups. The first one (II – V having an additional functional group in the position 2′) and the second one (compounds VI – VIII with supplementary substituents in the position 2 and 3 of the anthracene skeleton). Anthracene and 9-acetoxy-10(4′-acetoxy)phenylanthracene (I) are used as a standard.

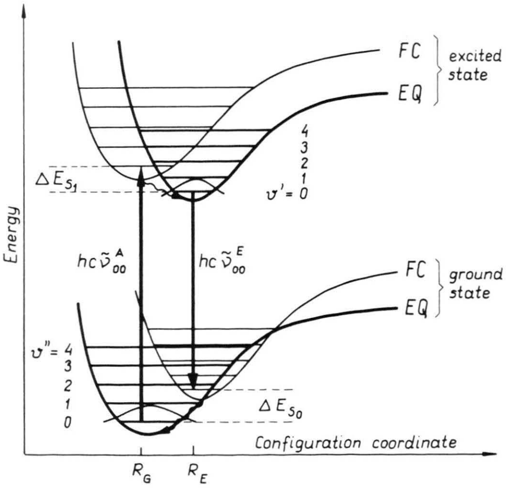


Fig. 2. The potential energy curves of an absorbing and emitting molecule in a solution.

From the spectra in Fig. 1 and the data in Table 1 it can be concluded that:

a) The loss of mirror relationship measured by ΔS^2 has values of 16 and 20% for the two groups of molecules, respectively. (For anthracene 8%). The differences are bigger than the estimated error (about 4%) caused by the decomposition of the spectra and the determination of the relative intensities.
b) The Stokes spectral shift of the first group of compounds is constant (within the error limit $\pm 50\ \mathrm{cm}^{-1}$); its value is bigger for the second group, where an increase with number of substituents is noticed.
c) The destabilization energy is distinctly bigger for the second group of molecules (about two times). This indicates a difference between the equilibrium nuclear configurations of the S_0 and S_1 states as well as a change of the equilibrium internuclear distances (R_{G} and R_{E} in Figure 2).
d) The correlation between the loss of the mirror relationship, the Stokes shift and the destabilization energy indicates a significant change of nuclear conformation (planarity) in the ground $\mathrm{S}_0\,(^1\mathrm{A}_{1g})$ and excited $\mathrm{S}_1\,(^1\mathrm{B}_{2u})$ states [16, 17]. The differences in the equilibrium geometries are bigger for the second group of molecules.

The small departure from the mirror symmetry justifies a description of the electronic states as for anthracene. The substituents influence the π-electrons of the ring as perturbers which do not change the symmetry group of the anthracene skeleton responsible for the radiation process. Its weak influence is recognized in the absorption and fluorescence spectra as a batochromic and steric effect.

3.2. *The ground state absorption spectra*

The dependence of the molar extinction coefficient on the wave number of the four selected compounds is presented in Figures 3 and 4. Between $25\,000 - 50\,000\ \mathrm{cm}^{-1}$ three electronic transitions can be distinguished, similar as for anthracene (see Fig. 5), namely the $\mathrm{S}_0\,(^1\mathrm{A}_{1g}) \rightarrow \mathrm{S}_1\,(^1\mathrm{B}_{2u})$ (in the $25\,000 - 32\,000\ \mathrm{cm}^{-1}$ spectral region), $\mathrm{S}_0\,(^1\mathrm{A}_{1g}) \rightarrow \mathrm{S}_2\,(^1\mathrm{B}_{3u})$ (in the $38\,000 - 41\,000\ \mathrm{cm}^{-1}$ region) and $\mathrm{S}_0\,(^1\mathrm{A}_{1g}) \rightarrow \mathrm{S}_3\,(^1\mathrm{B}_{1g})$ ($45\,000 - 48\,000\ \mathrm{cm}^{-1}$). Table 2 (column 2 and 3) collects the 0 – 0 vibrational frequencies of the corresponding electronic transitions

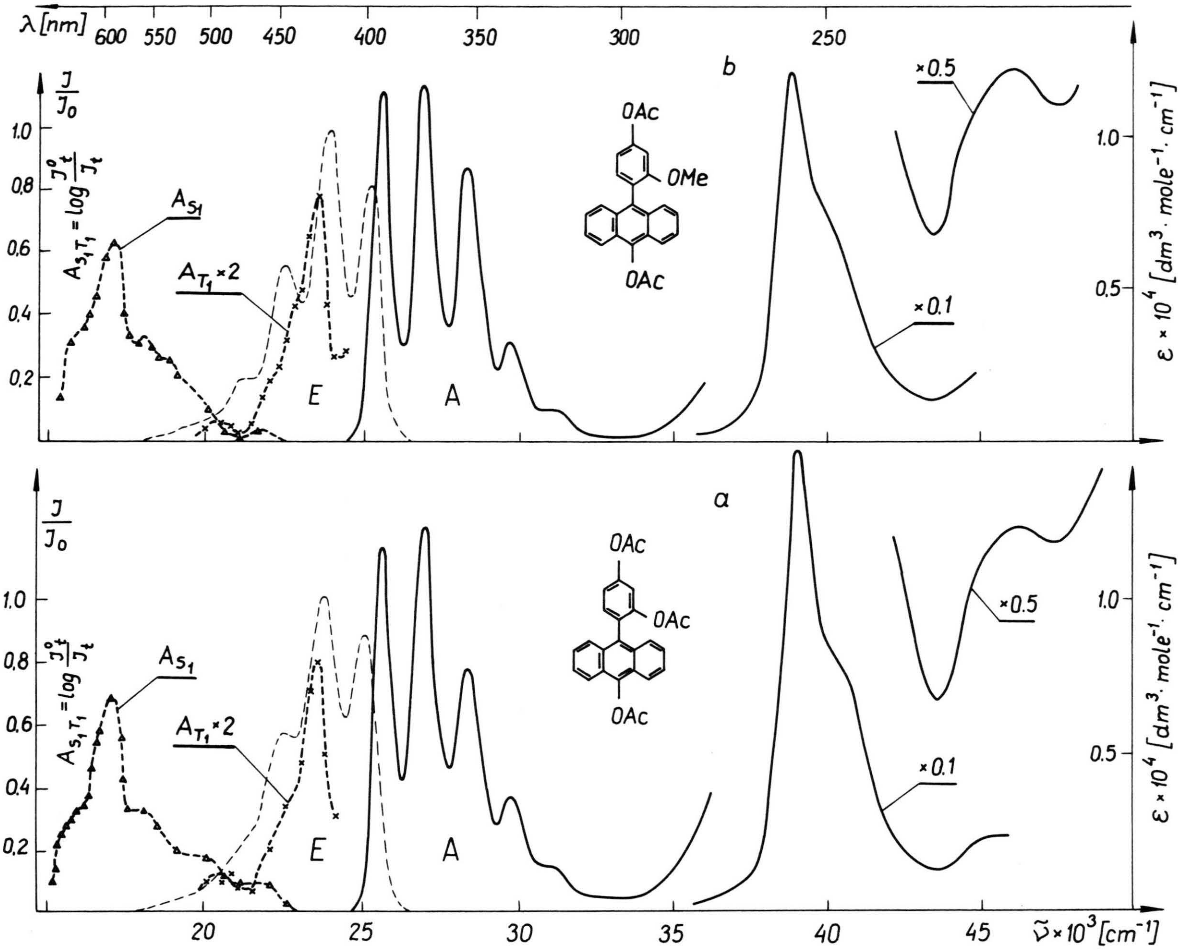


Fig. 3. The ground- and excited-state absorption spectra of: a) 9-acetoxy-10(2′,4′-diacetoxy)phenylanthracene, b) 9-acetoxy-10(4′-acetoxy-2-′-metoxy)phenylanthracene in dioxane —— the $S_0 \to S_1$, S_2 and S_3 absorption curve, - - - normalised fuorescence spectrum, –△–△– $S_1 \to S_k$ (A_{S_1}) and –×–×– $T_1 \to T_n$ (A_{T_1}) absorbances spectra.

and their absorption cross sections. Comparing the obtained values with the respective data of anthracene (they are given in parentheses) one finds that they are shifted to longer wave lengths. The shifts with respect to the position of the 0–0 vibronic transition of anthracene are 1250, 750 and about 300 cm^{-1} for the first group of compounds. Compounds possessing additional functional groups in the positions 2 and 3 of the anthracene ring (second group of compounds) exhibit larger shifts of all three bands. They are particularly large for the $S_0 \to S_2$ and $S_0 \to S_3$ bands (800, 1000 and 1400 cm^{-1} for the $S_0 \to S_2$ band and 1000, 1100 and 3000 cm^{-1} for the $S_0 \to S_3$ band of the compounds VI, VII and VIII, respectively). These shifts occur because the electronic transition moment responsible for those bands is parallel to the longer axis of the molecule.

The analysis of the absorption cross sections ($\sigma(\tilde{\nu}) = 3.81 \cdot 10^{-17} \varepsilon(\tilde{\nu})$) indicates that the substituents in compounds of the first and partly of the second group cause a 12% and 30% increase of the $\sigma(\tilde{\nu})$ value for the $S_0 \to S_1$ and $S_0 \to S_3$ bands and a 20% decrease in the $S_0 \to S_2$ band with respect to anthracene. It must be noted that the acetoxy and metoxy groups substituted at positions 2 and 3 of the anthracene skeleton influence the ground state absorption spectra otherwise. The intensities of the two first bands are significantly weaker, and for the $S_0 \to S_3$ band stronger than those of anthracene. These findings confirm that for this class of com-

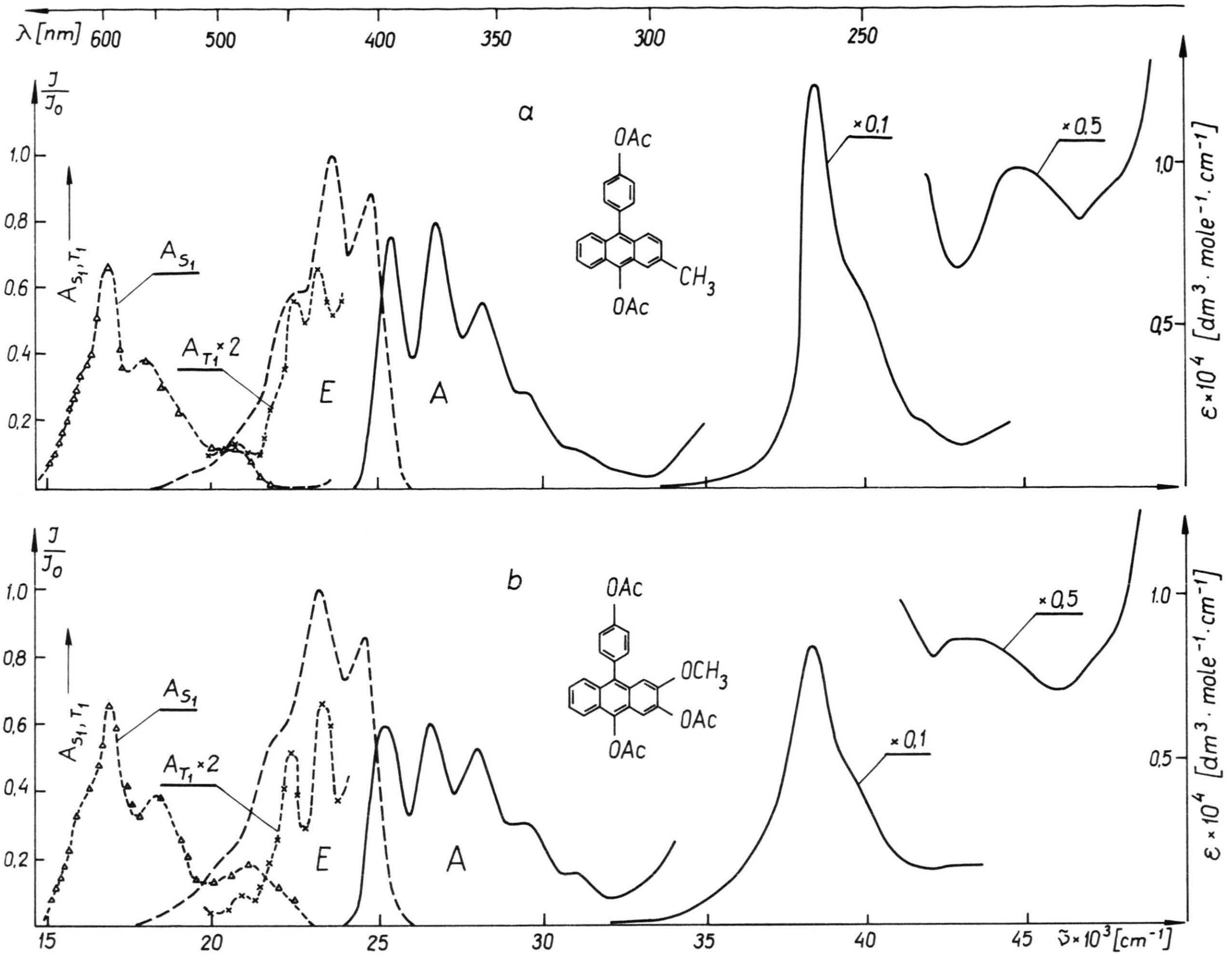


Fig. 4. The ground and excited state absorption spectra of: a) 2-mehyl-9-acetoxy-10(4′-acetoxy)phenylanthracene and b) 3-metoxy-2,9-diacetoxy-10(4′-acetoxy)phenylanthracene in dioxane (marked as in Figure 3).

pounds the intensity of the absorption bands depends mainly on the position of substitution and the kind of the functional group substituted in the anthracene ring.

3.3. *The excited state absorption spectra*

In Figs. 3 and 4 dashed curves with triangles and crosses give the excited singlet, $A_{S_1}(\tilde{\nu})$, and excited triplet, $A_{T_1}(\tilde{\nu})$, absorbances of the compounds in dioxane solution at the room temperature. These spectra are averaged over five measurements. The maximum deviation between measurements was $< 20\%$ even when data were obtained from samples in different experimental runs. The absorbance spectra $A_{S_1}(\tilde{\nu})$ and $A_{T_1}(\tilde{\nu})$ have been deconvoluted into three peaks of different intensity. Their absorption cross sections and wave numbers are collected in Table 2, column 3 and 4. The corresponding data for anthracene are given in parenthesis.

Scrutinizing the absorption spectra of triplet states it can be concluded that functional groups as well as their location in the phenyl ring do not influence the intensities and positions of the vibrational peaks. Weak auxochromes additionally introduced into positions 2 and 3 of the anthracene ring cause a small change of the peak positions (a batochromic shift with respect to the parent hydrocarbon, see Fig. 5) and an intensity decrease of the peak at 23300 cm^{-1}. The intensity of the second peak at about 22400 cm^{-1} remains unchanged with-

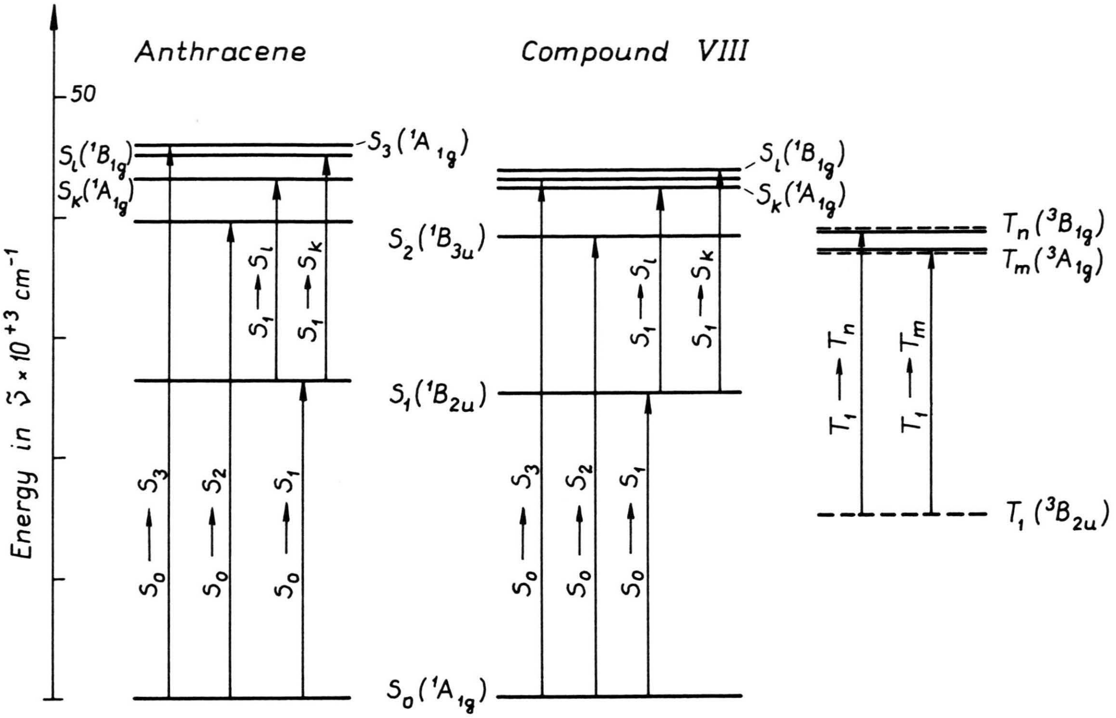


Fig. 5. The Jabłoński energy-level diagram of anthracene and 3-methoxy-2,9-diacetoxy-10(4′-acetoxy)phenylanthracene with indication of the transitions studied. The positions of the triplet levels of anthracene (dotted lines) are taken from [18]. The positions of the T_m and T_n levels of the compound VIII (full lines) are given under the assumption that the T_1-level has the same energy value as anthracene.

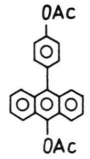
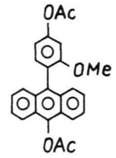
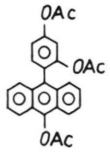
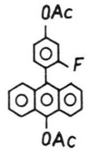
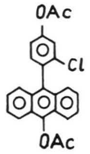
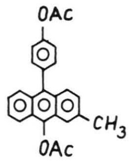
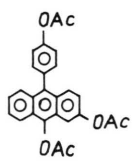
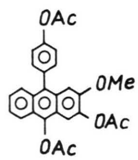
in the limit of the experimental error of the $A_{T_1}(\tilde{\nu})$ determination. The intensity behaviour of those two peaks suggests that the peaks belong to a different electronic transition. In accordance with the classification discussed for anthracene in [18, 19], these two peaks belong to the $T_1(^3B_{2u}) \rightarrow T_m(^3A_{1g})$ and $T_1(^3B_{2u}) \rightarrow T_n(^3B_{1g})$ transitions, respectively. The transition moments of those bands are parallel to the shorter (a) and longer (b) axis of the molecules. There is an exception for the molecule IV, for which the triplet absorption cross sections of both electronic transitions are smaller than for the corresponding other compounds.

It must be noticed that the maximal σ_{T_1} at 23400 cm^{-1} is about four times smaller than that of anthracene. This makes the $T_1 \rightarrow T_n$ absorption measurements more difficult.

As it was mentioned, the $S_1 \rightarrow S_k$ absorbance spectra were also deconvoluted into three peaks. The long-wave peak is responsible for the $S_1(^1B_{2u}) \rightarrow S_k(^1A_{1g})$ transition. This transition is hipsochromically shifted by 400 cm^{-1} with respect to the corresponding band in anthracene (see Figure 5). The intensity is constant within the limits of the experimental error and is slightly weaker than in the case of anthracene (the average absorption cross-section for all compounds is $(3.60 \pm 0.24)\ 10^{-17}$ cm^2 whereas it is for anthracene $(3.80 \pm 0.36)\ 10^{-17}$ cm^2. The second peak at about 18000 cm^{-1} corresponds to the $S_1(^1B_{2u}) \rightarrow S_l(^1B_{1g})$ transition and is hipsochromically shifted by about 200 cm^{-1} with respect to anthracene. The intensity of this peak is 25% smaller than for anthracene. The third peak at 20100 cm^{-1} is very weak and needs further studies before it can be discussed.

It follows from theoretical studies [18, 19] that the transition moments of the two identified peaks are parallel to the longer and shorter axis of the mole-

Table 2. Cross sections for absorption from S_1- and T_1-states and their peak frequencies for the substituted derivatives of 9-acetoxy-10(4′-acetoxy)phenylanthracene in dioxane. The values for anthracene, given in parantheses, were used as a standard.

Transition		$S_0(A_{1g}) \rightarrow \left\{\begin{array}{l} S_1(^1B_{2u})^a \\ S_2(^1B_{3u})^b \\ S_3(^1A_{1g})^b \end{array}\right.$		$S_1(^1B_{2u}) \rightarrow \left\{\begin{array}{l} S_k(^1A_{1g})^b \\ S_l(^1B_{1g})^a \end{array}\right.$		$T_1(^3B_{2u}) \rightarrow \left\{\begin{array}{l} T_m(^3A_{1g})^b \\ T_n(^3B_{1g})^a \end{array}\right.$	
Compounds		$\tilde{\nu}$ [cm^{-1}]	σ [10^{-17} cm^2]	$\tilde{\nu}$ [cm^{-1}]	σ [10^{-17} cm^2]	$\tilde{\nu}$ [cm^{-1}]	σ [10^{-17} cm^2]
I		25 500	4.01	17 050	3.97	20 250	
		(26 750)	(3.60)	(16 650)	(3.80)	(21 000)	(1.82)
		38 950	50.41	18 400	1.67	22 250	3.72
		(39 650)	(68 74)	(18 200)	(2.41)	(22 600)	(3.34)
		45 800	8.10	21 800		23 400	9.16
		(46 000)	(5.79)	(21 400)		(23 550)	(25.04)
II		25 500	4.28	17 000	3.41	20 500	
		38 850	45.82	18 500	1.43	22 250	2.30
		46 000	9.39	20 100		23 450	7.99
III		25 500	4.43	17 050	3.33	20 700	
		38 900	56.52	18 250	1.06	22 150	2.22
		46 000	9.55	20 100		23 400	8.55
IV		25 500	4.66	17 000	3.63	20 800	
		38 900	61.10	18 200	1.87	22 250	1.87
		45 500	8.63	20 000		23 450	5.75
V		25 500	4.77	17 000	3.65	20 500	
		39 000	49.10	18 350	1.86	22 300	3.36
		45 500	10.30	20 100		23 450	7.20
VI		25 500	4.28	16 950	3.76	20 700	1.05
		38 850	45.82	18 150	2.10	22 550	3.90
		45 000	9.39	20 100		23 250	5.43
VII		25 400	2.94	17 000	3.38	20 500	1.03
		38 650	51.93	18 250	1.79	22 150	3.52
		44 900	9.47	20 000		23 100	4.73
VIII		25 200	2.27	17 050	3.51	20 800	0.57
		38 250	31.70	18 400	1.85	22 400	3.18
		43 000	6.49	20 300		23 350	4.04

cules. The observed shifts and intensity changes do not allow us to draw conclusions on the correlations between the kind of substituents, position of the substitution and the changes of the energy value of the high-lying electronic states.

Further measurements could give more precise data helpful in the classification of the separate electronic transitions in the excited absorption spectra.

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