Substituted Derivatives of 10-Phenyl-9-Acetoxyanthracene

Janina Heldt, Józef Heldt * and Janina Gronowska **
Institute of Physics, University of Gdańsk, Gdańsk, Poland

(Z.Naturforsch. **30 a**, 612 – 618 [1975]; received March 3, 1975)

Absorption and Emission Spectra, Quantum Yield and Lifetime of Fluorescence

The absorption and fluorescence spectra of five substituted derivatives of 10-phenyl-9-acetoxyanthracene were measured and the oscillator strengths of the $^1A \rightarrow {}^1L_a$, $^1A \rightarrow {}^1B_b$ and $^1A \rightarrow {}^1C_b$ electronic vibration bands were determined. Comparison of the absorption spectra of these compounds to the unsubstituted molecule (anthracene) indicate the presence of bathochromic and steric effects. The fluorescence quantum yield and the mean lifetime of the fluorescence were also measured.

1. Introduction

The replacement of one or more hydrogen atoms by some functional groups in a polynuclear aromatic compound modifies the electronic absorption spectrum in a complex manner. In the literature [1–3] four types of these substitution effects are recognized. Usually they are designated as: a. the bathochromic effect (B-effect), b. the fine structure effect (Fs-effect), c. the conjugation effect (C-effect) and d. the steric effect (S-effect). The substitution effects have been investigated for many derivatives of conjugated molecules [1–6]. The theory of these effects has been described in quantum chemistry books, e. g. [7, 8].

In this paper we present the results of studies of the substitution effects on five derivatives of 10-phenyl-9-acetoxyanthracene (I) namely:
10-(4-acetoxyphenyl)-9-acetoxyanthracene (II),
10-(4-methylphenyl)-9-acetoxyanthracene (III),
10-(4-acetoxyphenyl)-2,9-diacetoxyanthracene (IV),
10-phenyl-2-methyl-9-acetoxyanhtracene (V) and
10-(2-acetoxyphenyl)-3-metoxy-2,9-diacetoxyanthracene (VI).

In order to illustrate the influence of the substituents $-OCOCH_3(-OAc)$, $-OCH_3$ and $-CH_3$ at different positions on the anthracene or phenyl ring on the absorption and emission transition probabilities the oscillator strength, f, has been computed for the $^1A \rightarrow {}^1L_a$, $^1A \rightarrow {}^1B_b$ and $^1A \rightarrow {}^1C_b$ bands. Also the mean lifetime τ and the quantum yield Q of the fluorescence have been measured.

2. Experimental

The synthesis of the investigated compounds is given in [9]. The compounds were recrystallized from ethanol and their purity was checked chromatographically before use. The solvent n-heptane was spectrally pure. The concentration of the compounds in the solution was $2 \times 10^{-5}\ g \cdot cm^{-3}$.

The absorption spectra were measured on the Perkin-Elmer Type 402 and the Zeiss-Jena type VSU-2 spectraphotometers. The emission pectra were obtained by means of photoelectric recording as shown in Figure 1. The fluorescence was excited by irradiation with light emitted by a 100 W bulb filtered by means of a Hg-monochromatfilter with maximum transmission at 365 nm.

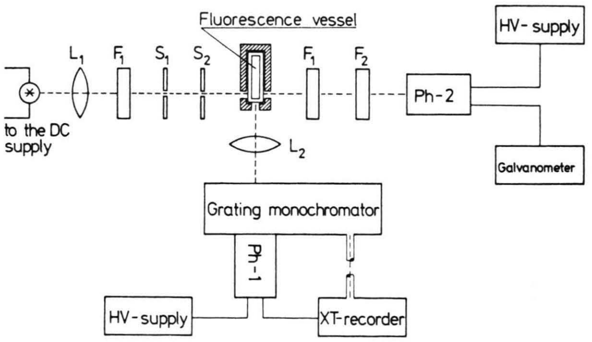


Fig. 1. Schematic diagram of the experimental set-up. L_1, L_2 – lenses, S_1, S_2 – slits, $F_1 \dots F_3$ – filters, Ph-1, Ph-2 – photomultipliers.

Reprint requests to Doc. Dr. hab. J. Heldt, Institut Fizyki, Uniwesytet Gdański, *Gdańsk*, Poland.

---

* Now on leave from the University of Gdańsk (Poland) at I. Physikalisches Institut der Universität zu Köln, *D-5000 Köln 41*, Fed. Rep. of Germany.

** Institute of Chemistry, N. Copernicus University, *87-100 Toruń*, Poland.

The quantum yield of the solutions under investigation was measured by means of two photomultipliers (see Fig. 1), one monitoring the intensity of the transmitted beam and the other (set perpendicularly to the former) the intensity of the fluorescence light. The solutions were excited in the long-wave absorption band as in the case of emission spectra measurements. The photocurrents from photomultipliers Ph-1 and Ph-2 were measured by means of an XT recorder and a mirror galvanometer, respectively. The apparatus for measuring the fluorescence quantum yield was calibrated by means of a solution of anthracene in n-hexane for which the quantum yield is well known[10].

The fluorescence lifetime measurements for the n-heptane solutions of these compounds were performed by means of a phase shift fluorometer constructed by Bauer and Kowalczyk[11]. In the apparatus, solutions are excited with a HBO-200 mercury lamp through a monochromator transmitting the 365 nm Hg line. The emission was observed through a second monochromator at 405 nm, i. e., at the first vibration peak of the emission spectrum. The quantum yield and decay time of the solutions were measured several times. The figures given in Table 1 are mean values of five measurements performed at intervals of several days. The instrumental errors of the mean lifetime and the quantum yield are ± 0.1 ns and ± 0.05, respectively.

The results of spectral investigations are shown in Figures 2, 3 and 5. The positions of the vibrational sublevel maxima of the absorption and emission spectra, values of the molar extinction coefficient ε, quantum yield Q and the mean lifetime τ of fluorescence are presented in Table 1. The fluorescence spectra are normalized to the maximal value. The above measurements were carried out at room temperature.

3. Results and Discussion

The absorption spectra of the compounds are presented in Figures 2 and 3, and their structural formulas are given in Figure 4 and Table 1. In Figs. 2 and 3 the absorption spectra of the compounds II – VI are compared to those of 10-phenyl-9-acetoxyanthracene, (I), reported in our earlier paper[5]. The spectra of these compounds are similar in shape and intensity to the spectrum of the unsubstituted hydrocarbon (anthracene), but the whole curve is shifted to longer wave lengths. Hence they exhibit the bathochromic effect. In the absorption spectrum, in analogy with anthracene, three separate bands related to three different electronic transitions can be distinguished. They can be designated as ${}^1A \rightarrow {}^1L_a$, ${}^1A \rightarrow {}^1B_b$ and ${}^1A \rightarrow {}^1C_b$ transition using the Platt notation[3]. Hereafter, for abbreviation, the bands are designated as ${}^1L_a$, ${}^1B_b$ and ${}^1C_b$. The above bands consist of several vibrational peaks of different intensities (see Table 1).

As can be seen from Figs. 2 and 3 the magnitudes of the band shifts depend on the substituents and their position in the ring system. The introduction of $-\mathrm{OCOCH_3}$, $-\mathrm{C_6H_5}$, 4-acetoxyphenyl and 4-methylphenyl groups in positions 9 and 10 of the anthracene ring causes a change of electric transition moments, mainly of the one which is parallel to the shorter axis of the molecule. These changes give rise to shifts of the $0-0$ electronic vibration transitions. The observed shifts show a higher value in the case of the ${}^1L_a$ band and a lower one in the case of the ${}^1B_b$ and ${}^1C_b$ bands. These frequency shifts calculated with respect to the anthracene values for the ${}^1L_a$ and ${}^1B_b$ bands are: 950 and 500 $\mathrm{cm^{-1}}$ for compound I; 1100 and 650 $\mathrm{cm^{-1}}$ for compound II and 1200 and 800 $\mathrm{cm^{-1}}$ for compound III, respectively. The acetoxy and methyl groups additionally substituted in position 2 of the anthracene ring (compounds IV and V) cause extra shifts, which, calculated with regard to the values of $0-0$ electronic vibration transitions of the ${}^1L_a$ and ${}^1B_b$ bands of compounds II and I, are: 150 and 400 $\mathrm{cm^{-1}}$ and 200 and 650 $\mathrm{cm^{-1}}$, respectively. Note that the band shifts in the latter case show an opposite behaviour, i. e., the shift of the ${}^1B_b$ band is about three times larger than the one for the ${}^1L_a$ band, whereas in the case of compounds I, II and III, the shifts of the ${}^1L_a$ band are about twice those of the ${}^1B_b$ band. Since the ${}^1C_b$ band of the molecules is blurred and, furthermore, has only a weakly marked vibration structure, the frequency of the $0-0$ electronic vibration transition given in Table 1 is not exact. However, it should be emphasized that the ${}^1C_b$ band of all compounds investigated is shifted to the longer wave lengths like the ${}^1L_a$ and ${}^1B_b$ bands.

The shifts of the ${}^1L_a$, ${}^1B_b$ and ${}^1C_b$ bands in the absorption spectrum of compound VI agree with the above considerations.

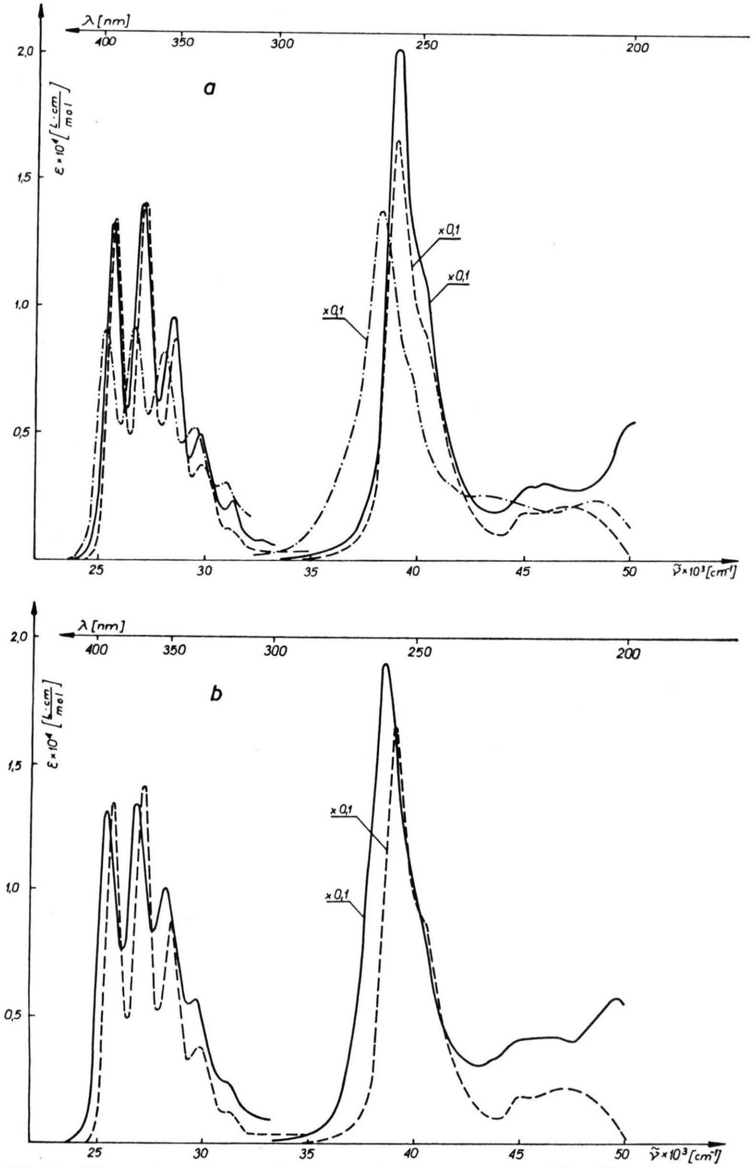


Fig. 2. Absorption spectra of compounds: I ——— (2 a, 2 b) ; II ——— (2 a) ; VI –·–·– (2 a) and IV ——— (2 b). The scale of the spectra in the UV are ten times smaller.

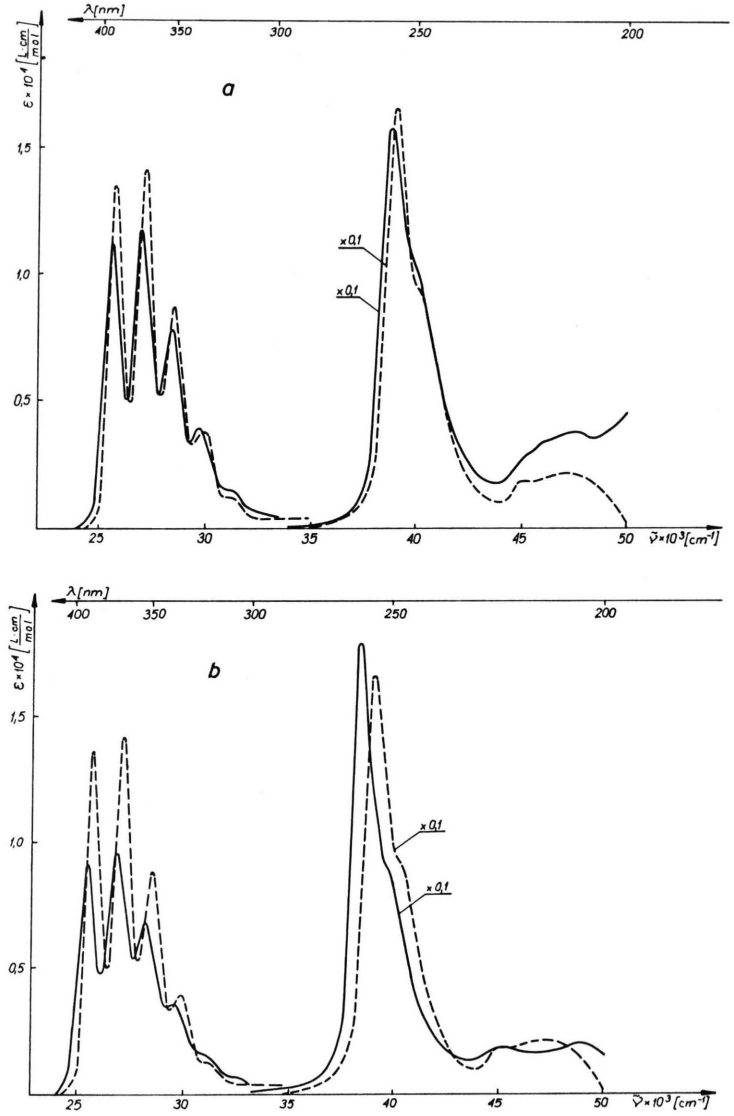
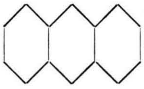
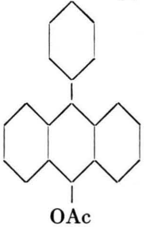
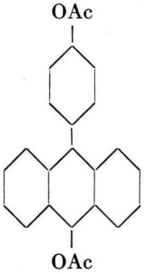
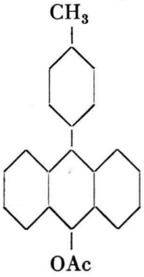
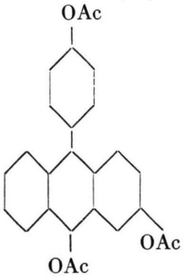
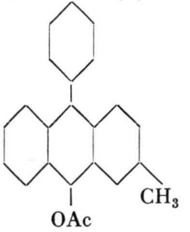
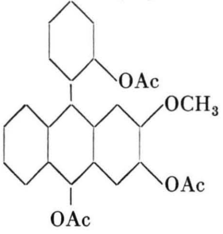


Fig. 3. Absorption spectra of compounds: I ——— (3 a, 3 b) ; III ——— (3 a) and V ——— (3 b). The scale of the spectra in the UV is ten times smaller.

Table 1. Position of absorption and emission maxima, the oscillator strengths, the quantum yield and the mean lifetime of fluorescence of the substituted derivatives of 10-phenyl-9-acetoxyanthracene.

Compound	Transition	Oscillator strength f	Quantum Yield Q Mean lifetime τ [ns]	Frequencies of the vibration peaks			
				Absorption		Emission	
				ε [$\mathrm{l\,mol^{-1}\,cm^{-1}}$]	ν_{ab} [$\mathrm{cm^{-1}}$]	I/I_{max}	ν_{fl} [$\mathrm{cm^{-1}}$]
Anthracene 	$^1A \rightleftarrows {}^1L_a$	0.16	0.31	9 400	26 700	0.58	26 450
				9 500	28 150	1.00	25 150
				6 800	29 600	0.39	23 800
				3 500	31 000	0.11	22 500
			3.40	1 500	32 350	0.02	21 200
				900	33 800		
	$^1A \rightarrow {}^1B_b$	2.54		181 000	39 600		
				95 000	41 000		
	$^1A \rightarrow {}^1C_b$	0.33		13 600	45 400		
10-Phenyl-9-acetoxy-anthracene (I) 	$^1A \rightleftarrows {}^1L_a$	0.25	0.59	13 500	25 750	1.00	24 900
				14 200	27 200	0.92	23 700
				8 700	28 550	0.44	22 400
			5.40	3 700	29 850	0.11	21 100
				1 200	31 200	0.02	19 500
	$^1A \rightarrow {}^1B_b$	2.30		166 000	39 100		
				85 000	40 400		
	$^1A \rightarrow {}^1C_b$	0.79		18 500	44 690		
10-(4-Acetoxy-phenyl)-9-acetoxy-anthracene (II) 	$^1A \rightleftarrows {}^1L_a$	0.26	0.56	13 200	25 600	1.00	24 900
				14 000	26 950	0.90	23 700
				9 500	28 400	0.36	22 200
				4 900	29 750	0.11	20 750
			5.40	2 300	31 250	0.04	19 500
				700	32 700		
	$^1A \rightarrow {}^1B_b$	2.80		211 100	38 950		
				100 000	40 350		
	$^1A \rightarrow {}^1C_b$	0.90		29 000	45 200		
				30 050	46 000		
10-(4-Methyl-phenyl)-9-acetoxy-anthracene (III) 	$^1A \rightleftarrows {}^1L_a$	0.24	0.55	11 300	25 500	1.00	25 150
				11 800	26 900	0.93	24 000
				7 800	28 300	0.45	22 750
			5.30	3 800	29 700	0.15	21 250
				1 500	31 200	0.03	19 850
	$^1A \rightarrow {}^1B_b$	2.70		158 000	38 800		
				94 000	40 200		
	$^1A \rightarrow {}^1C_b$	0.86		26 000	45 100		
				38 000	47 000		

Compound	Transition	Oscillator strength f	Quantum Yield Q Mean lifetime τ [ns]	Frequencies of the vibration peaks			
				Absorption		Emission	
				ε [$\mathrm{lmol^{-1}\,cm^{-1}}$]	ν_{ab} [$\mathrm{cm^{-1}}$]	$I/I_{\max}$	ν_{fl} [$\mathrm{cm^{-1}}$]
10(4-Acetoxyphenyl)-2,9-diacetoxyanthracene (IV)							
	$^1A \rightleftarrows {}^1L_a$	0.23	0.36	13 200	25 450	1.00	24 700
				13 400	26 850	0.87	23 450
				10 100	28 200	0.38	22 000
			5.90	5 600	29 600	0.14	20 700
				2 200	31 150	0.04	19 150
	$^1A \rightarrow {}^1B_b$	2.47		190 000	38 550		
				97 500	40 000		
	$^1A \rightarrow {}^1C_b$	0.76		32 000	44 600		
				58 200	49 700		
10-Phenyl-2-methyl-9-acetoxyanthracene (V)	$^1A \rightleftarrows {}^1L_a$	0.21	0.52	9 000	25 450	1.00	24 700
				9 500	26 850	0.88	23 450
				6 900	28 150	0.43	22 250
				3 000	29 550	0.13	20 650
			5.50	1 400	30 900	0.04	19 250
				600	32 400		
	$^1A \rightarrow {}^1B_b$	2.34		180 400	38 450		
				84 500	39 850		
	$^1A \rightarrow {}^1C_b$	0.79		18 500	45 000		
				20 500	49 000		
10-(2-Acetoxyphenyl)-3-metoxy-2,9-diacetoxyanthracene (VI)	$^1A \rightleftarrows {}^1L_a$	0.25	0.37	9 100	25 250	1.00	24 550
				9 200	26 600	0.91	23 250
				8 300	28 050	0.48	21 900
			6.60	5 200	29 450	0.17	20 500
				3 000	30 900	0.04	19 000
	$^1A \rightarrow {}^1B_b$	2.34		139 000	38 250		
				60 500	39 750		
	$^1A \rightarrow {}^1C_b$	0.59		25 000	43 400		
				24 500	48 500		

It results from Fig. 2 and 3 (see also Table 1) that, when the hydrogen atoms in the anthracene ring are replaced by phenyl, acetoxy- and methylphenyl, $-\mathrm{OAc}$, $-\mathrm{CH_3}$ and $-\mathrm{OCH_3}$ groups, the absorption spectrum is modified in a complex manner, i. e. the substituents cause the bathochromic effect and change the intensities of the ^1L_a, ^1B_b and ^1C_b bands. In order to illustrate the influence of the above mentioned groups on the absorption transition probabilities the oscillator strengths of the three bands have been determined using the following expression[6]:

$$f = (3\,m\,c\,n/\pi\,e^2) \int \varepsilon_{\gamma\mathrm{M}}\,\mathrm{d}\gamma\,, \qquad (1)$$

where n is the refractive index of the solvent, $\int \varepsilon_{\gamma\mathrm{M}}\,\mathrm{d}\gamma$ is the experimental value of the absorption integral of the solution and m, e and c have their standard meaning. As has been shown earlier[12], Eq. (1) is valid in the case when the solvent, as an external physical medium, is considered to be continuous and structureless dielectric. For this reason the obtained f values can be used in qualitative interpretations only.

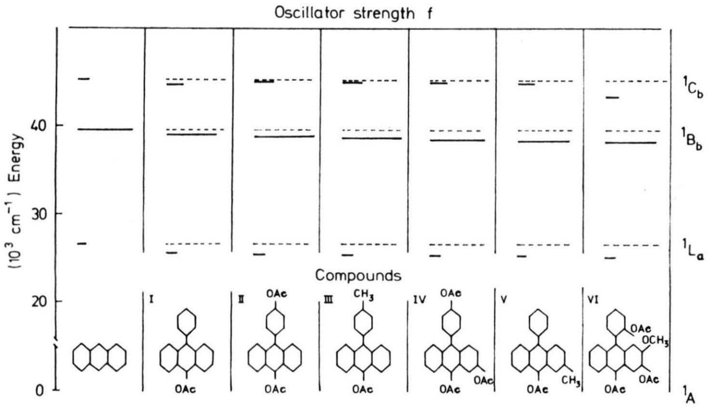


Fig. 4. The energy level scheme of the compounds investigated with marked values of oscillator strengths. The anthracene values are given for comparison only.

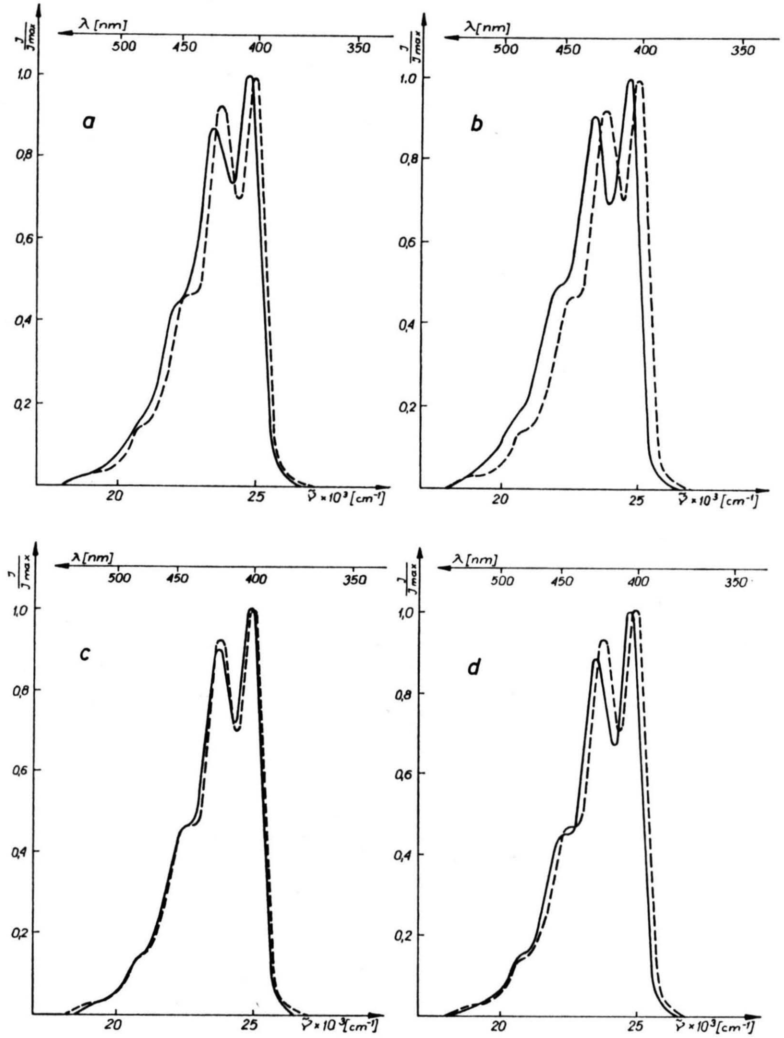


Fig. 5. The fluorescence spectra of compounds: I — — — (5 a, 5 b, 5 c, 5 d); IV ——— (5 a); VI ——— (5 b); II ——— (5 c) and V ——— (5 d).

The analysis of the *f* values (see Table 1) indicates that the substituents: phenyl, acetoxy- and methylphenyl, acetoxy, methyl and methoxy, as compared with anthracene, cause a double increase of the *f* value for the ^1L_a and ^1C_b bands and smaller changes for the ^1B_b band. It should be emphasized that the ^1C_b band, which in anthracene is presumed to be forbidden, has a larger absorption transition probability for the compounds investigated. This can be due to a small interaction of the two conjugated systems in the derivatives of 10-phenyl-9-acetoxyanthracene[7].

The determined energy values of the ^1L_a, ^1B_b and ^1C_b electronic states and their corresponding oscillator strengths are graphically presented in Fig. 4 where the anthracene data are included for comparison. In Figure 4 the length of the horizontal lines are proportional to the *f* values and their position on the energy scale gives the energy value of the lower electronic vibration transition.

The fluorescence spectrum of the compounds I, II, IV, V and VI are given in Figure 5. As can be seen from Fig. 5, the emission spectrum shows a less clear vibrational structure than the absorption spectrum. The intensity distribution of the vibration peaks of the emission spectrum differ from that in the ^1L_a absorption band. The absorption and emission spectra do not perform the so-called mirror symmetry. The frequency differences between neighbouring vibrational peaks are not equal; they have different values from those of anthracene. The obtained differences are larger than the experimental error in the determination of the frequencies. The estimated experimental error in the determination of the frequencies of the maxima varies between 40 cm^{-1} at the high frequencies and 20 cm^{-1} at the low frequencies. The absence of mirror symmetry, and the fact that the vibration structure of the absorption and emission spectrum is blurred, appears to be due to the weak interaction of the phenyl and anthracene derivatives in the compounds.

Column three of Table 1 contains the fluorescence quantum yield Q (upper number) and the mean lifetime τ (lower number) of the ^1L_a electronic state. The fluorescence quantum yields of the compounds I, II, III and V are about 40% larger than the value obtained for anthracene. The Q values determined for compounds IV and VI are also about 14% higher. The fluorescence of the compounds IV and VI (see Table 1) has a longer mean lifetime. It can cause bigger solvent quenching of the fluorescence than in the case of the other compounds. Also, it should be noted that the ratio Q/τ is constant for the compounds I, II, III and V and differs for the compounds IV and VI within the experimental error limit.

4. *Acknowledgement*

We wish to express our appreciation to Doz. Dr. R. Bauer for his help in the lifetime measurements. One of us (J. H.) wishes to thank Prof. Dr. H. Walther for the hospitality shown during his stay at the University of Köln. He also thanks the Alexander von Humboldt-Stiftung for a fellowship.

---

[1] N. Jones, J. Am. Chem. Soc. **67**, 2127 [1945].

[2] N. Jones, Chem. Rev. **41**, 353 [1947].

[3] Systematics of the Electronic Spectra of Conjugated Molecules: A Source Book by J. R. Platt and Co-workers, John Wiley and Sons, Inc., New York 1964.

[4] A. S. Cherkasov and T. M. Vember, Optika and Spektrosk. **1**, 663 [1956].

[5] Janina Heldt, Janina Gronowska, and Józef Heldt, Acta Phys. Polon. A **47**, 613 [1974].

[6] Th. Förster, Fluoreszenz Organischer Verbindungen, Göttingen 1951.

[7] C. Sandorfy, Die Elektronenspektren in der Theoretischen Chemie, Verlag Chemie GmbH., Weinheim 1961.

[8] Peter O'D. Offenhartz, Atomic and Molecular Orbital Theory, McGraw-Hill, New York 1970.

[9] Janina Gronowska and Janina Heldt, Roczniki Chem., in press.

[10] G. Weber and F. W. J. Teale, Trans. Faraday Soc. **53**, 646 [1957].

[11] R. K. Bauer and A. Kowalczyk, Raport techniczny Nr. 3, Nicholas Copernicus University, Toruń 1974.

[12] H. Grudzinski and J. Heldt, Acta Phys. Polon. **25**, 391 [1964].