

**9-ACETOXYANTHRACENE DERIVATIVES. PART IX.*
SYNTHESES AND SPECTRAL INVESTIGATIONS OF
9-ACETOXY-10-(ACETOXYHALOGENOPHENYL)ANTHRACENES**

By

J. GRONOWSKA, A. DZIELENDZIAK

Institute of Chemistry, N. Copernicus University, 87—100 Torun, Poland
and

J. HELDT

Institute of Physics, University, 80—952, Gdansk, Poland

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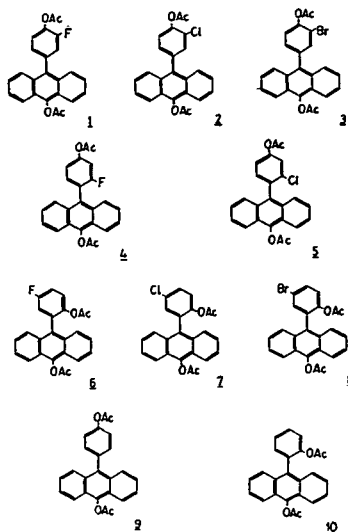
Some 9-acetoxy-10-(acetoxyhalogenophenyl)anthracenes have been synthesized. The influence of halogen substituents on the electronic absorption and emission spectra and the oscillator strength were investigated.

In previous papers [1—6] the influence of substituents such as $-\text{OCOCH}_3$, $-\text{OCH}_3$, $-\text{CH}_3$ on the electronic absorption and emission spectra of some derivatives of 9-acetoxy-10-phenyl-anthracene was investigated. It was found that mainly the π -electrons of anthracene ring were responsible for the formation of the spectra of these compounds.

In this paper we present data on the synthesis and the electronic absorption and emission spectra of new derivatives of 9-acetoxy-10-phenylanthracene:

9-acetoxy-10-(4'-acetoxy-3'-fluorophenyl)anthracene (1),
9-acetoxy-10-(4'-acetoxy-3'-chlorophenyl)anthracene (2),
9-acetoxy-10-(4'-acetoxy-3'-bromophenyl)anthracene (3),
9-acetoxy-10-(4'-acetoxy-2'-fluorophenyl)anthracene (4),
9-acetoxy-10-(4'-acetoxy-2'-chlorophenyl)anthracene (5),
9-acetoxy-10-(2'-acetoxy-5'-fluorophenyl)anthracene (6),
9-acetoxy-10-(2'-acetoxy-5'-chlorophenyl)anthracene (7) and
9-acetoxy-10-(2'-acetoxy-5'-bromophenyl)anthracene (8).

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The spectra of compounds 1—5 were compared with those of 9-acetoxy-10-(4'-acetoxyphenyl)anthracene (9), and those of 6—8 with those of 9-acetoxy-10-(2'-acetoxyphenyl)anthracene (10). The synthesis of fluoro compounds 1, 4 and 6 was described previously [7]. Compounds 2, 5 and 7 were obtained analogously to method [7], using *o*-, *m*- and *p*-chlorophenols in the reaction. Compounds 3 and 8 were prepared similarly, with the use of *o*- and *p*-bromophenols. The structures of new compounds 2, 3, 5, 7 and 8 were elucidated with physicochemical methods, *i.e.* through their degradation into anthraquinone [8] and PMR spectral analysis [9]. Moreover, elementary analysis of these compounds was carried out and their IR spectra were recorded.

From papers [10—13] it follows that heavy element substituents in aromatic hydrocarbons influence their absorption, emission and phosphorescent spectra, mainly by changing the probabilities of the intersystem crossing transitions. The above finding concerns the spin-orbital coupling of a heavy element with the π -electron cloud of the anthracene skeleton when a heavy element is substituted in the skeleton and is also found in other molecules of the environment, most often called "perturbators". In the present case, halogen is the substituent belonging to the conjugated system only weakly interacting with the π -electron cloud of the anthracene skeleton, which is responsible for the absorption and emission of light in the investigated part of the spectrum. In this connection rather small changes are to be expected in the values of the probabilities of the electronic transitions as well as in the values of the oscillatory peaks frequencies related to the vibrations of the anthracene skeleton atoms.

Experimental

All m.p.'s are corrected. Infrared (IR) spectra were measured in KBr discs on Zeiss Jena UR 20 spectrophotometer. Proton magnetic resonance (PMR) spectra were run with a Tesla BS 487C (80 MHz) spectrometer in deuterochloroform solution; tetramethylsilane (TMS, $\delta=0.00$ ppm) was applied as internal standard.

3-Phenyl-3-(halogenohydroxyphenyl)phtalides a-e

To a melting mixture of 0.050 mole of 2-benzoylbenzoic acid and 0.052 mole of the appropriate halogenophenol, 6 g of anhydrous $ZnCl_2$ was added. The reaction mixture was heated on an oil bath for *ca.* 8–10 h at 120–125 °C (in the case of 3- and 4-chlorophenol at 135–140 °C). The melt was dissolved in hot AcOH and the solution was poured into water. The white, amorphous precipitate was filtered off, washed well with water, extracted with 15% Na_2CO_3 aq., filtered off again and washed several times with water. The precipitate yielded colourless crystals from EtOH or AcOH after recrystallizations. For results *cf.* Table I.

Methyl ethers of phtalides a-e (aa-ea)

A mixture of 0.003 mole of phtalide **a-e**, 50 cm³ Me_2CO , 3 cm³ CH_3I and 2 g K_2CO_3 was boiled under reflux for 5 h. The reaction mixture was poured into water. The crude precipitate was filtered off and washed with water. The precipitate yielded colourless crystals after recrystallizations from EtOH. For results *cf.* Table I.

Acetates of phtalides a-e (ab-eb)

A sample of 0.005 mole of phtalide **a-e** was treated with 15 cm³ of Ac_2O and *ca.* 1.5 g of anhydrous $AcONa$ and heated for 3 h on an oil-bath at 120 °C. Then the mixture was poured into water. The precipitate was filtered off, washed with water and recrystallized several times from EtOH. For results *cf.* Table I.

2-Halogenohydroxybenzhydrylbenzoic acids (ac-ec)

A sample of 0.01 mole of phtalide **a-e** was reduced with 5 g of Zn dust in 100 cm³ of 80% AcOH for 7–10 h, with heating under a reflux condenser until the TLC showed the absence of phtalide. After filtration, the solution was poured into 800 cm³ of water. The white, amorphous precipitate was filtered off, washed with water and recrystallized from AcOH or EtOH. For results *cf.* Table I.

Acetates of 2-benzhydrylbenzoic acids ac-dc (ad-dd)

A mixture of 2-benzhydrylbenzoic acid **ac-dc** (0.002 mole) and 15 cm³ of Ac_2O was heated for 3 h at 120 °C. Then the solution was poured into water, giving the crude acetate. The product was recrystallized from EtOH aq. in each case. For results *cf.* Table I.

Benzhydrylbenzoic acid **ec** (from 4-bromophenol) gives ϵ -lactone with Ac_2O *ef.*

Table 1

Results of elemental analyses, yields, *m.p.*'s and IR spectra of phthalides **a-e**, their methyl ethers **aa-ea** and acetates **ab-eb**, 2-benzhydrylbenzoic acids **ac-ec**, acetates of acids **ad-dd**, and ϵ -lactones **dc-ec**

No	Compound	Formula, molecular mass	Analyses, %		Yield, %	M.p., °C	IR spectra, ν , cm^{-1}
			Calc.	Found			
1	2	3	4	5	6	7	8
1	3-Phenyl-3-(3'-chloro-4'-hydroxyphenyl)-phthalide (a)	$\text{C}_{20}\text{H}_{13}\text{ClO}_3$ 336.5	C 71.0 H 3.9 Cl 10.5	C 71.2 H 4.0 Cl 10.3	78	160.8—162.5 from EtOH	1740s (C=O, γ -lactone), 1130s (OH, phenol), 985m (C—O—C, γ -lactone);
2	Methyl ether of phthalide a (aa)	$\text{C}_{21}\text{H}_{15}\text{ClO}_3$ 350.5	C 71.9 H 4.3 Cl 10.1	C 71.9 H 4.7 Cl 9.9	74	120.5—122.0 from EtOH	2840w (CH_3 , methyl ether), 1380w (CH_3 , ether), 1260s (C—O—C, ether);
3	Acetate of phthalide a (ab)	$\text{C}_{22}\text{H}_{15}\text{ClO}_4$ 337.5	C 69.8 H 4.0 Cl 9.4	C 69.9 H 4.3 Cl 9.7	86	171.9—173.1 from EtOH	1770s (C=O, acetate), 1385s (CH_3 , acetate), 1195s (C—O—C, acetate);
4	2-(3'-Chloro-4'-hydroxybenzhydryl) benzoic acid (ac)	$\text{C}_{20}\text{H}_{15}\text{ClO}_3$ 338.8	C 70.9 H 4.4 Cl 10.5	C 70.7 H 4.6 Cl 10.3	80	172.2—174.4 from AcOH aq.	2710w (OH, dimer COOH), 1690s (C=O, COOH), 1180s (OH, phenol);
5	Acetate of acid ac (ad)	$\text{C}_{22}\text{H}_{17}\text{ClO}_4$ 380.8	C 69.4 H 4.5 Cl 9.4	C 69.1 H 4.8 Cl 9.0	81	177.8—178.8 from EtOH aq.	1770s (C=O, acetate), 1380s (CH_3 , acetate), 1150w (C—O—C, acetate);
6	3-Phenyl-3-(3'-bromo-4'-hydroxyphenyl)-phthalide (b)	$\text{C}_{20}\text{H}_{13}\text{BrO}_3$ 381.1	C 63.0 H 3.4 Br 21.0	C 63.3 H 3.3 Br 21.0	75	168.3—169.4 from AcOH	1740s (C=O, γ -lactone), 1140 m (OH, phenol), 975m (C—O—C, γ -lactone);
7	Acetate of phthalide b (bb)	$\text{C}_{22}\text{H}_{15}\text{BrO}_4$ 423.1	C 62.4 H 3.5 Br 18.7	C 62.6 H 3.4 Br 18.5	84	165.0—166.1 from EtOH	1765s (C=O, acetate), 1380s (CH_3 , acetate), 1200s (C—O—C, acetate);
8	2-(3'-Bromo-4'-hydroxybenzhydryl) benzoic acid (bc)	$\text{C}_{20}\text{H}_{15}\text{O}_3\text{Br}$ 383.2	C 62.7 H 3.9 Br 20.7	C 62.5 H 3.9 Br 20.9	75	164.7—166.1 from AcOH aq.	2660w (OH, dimer COOH), 1685s (C=O, COOH), 1185s (OH, phenol);
9	3-Phenyl-3-(2'-chloro-4'-hydroxyphenyl)-phthalide (c)	$\text{C}_{20}\text{H}_{13}\text{ClO}_3$ 350.5	C 71.0 H 3.9 Cl 10.5	C 71.4 H 4.3 Cl 10.5	70	233.4—234.6 from AcOH aq.	1735s (C=O, γ -lactone), 1220m (OH, phenol), 965m (C—O—C, γ -lactone);
10	Methyl ether of phthalide c (ca)	$\text{C}_{21}\text{H}_{15}\text{ClO}_3$ 350.5	C 71.9 H 4.3 Cl 10.1	C 72.0 H 4.5 Cl 10.0	84	191.5—193.0 from EtOH	2850w (CH_3 , methyl ether), 1375w (CH_3 , ether), 1260s (C—O—C, ether);

11	Acetate of phthalide c (cb)	$C_{22}H_{15}ClO_4$ 378.5	C 69.8 H 4.0 Cl 9.4	C 70.2 H 4.4 Cl 9.1	75	185.8—187.2 from EtOH	1755s (C=O, acetate), 1385s (CH ₃ , acetate), 1195s (C—O—C, acetate);
12	2-(2'-Chloro-4'-hydroxy-benzhydryl)benzoic acid (cc)	$C_{20}H_{15}ClO_3$	—	—	80	—	white amorphous substance, but its derivatives cd and 5 are crystalline
13	Acetate of acid cc (cd)	$C_{22}H_{17}ClO_4$ 380.8	C 69.4 H 4.5 Cl 9.4	C 69.2 H 4.7 Cl 9.2	81	219.8—221.2 from EtOH aq.	1760s (C=O, acetate), 1375s (CH ₃ , acetate), 1150m (C—O—C, acetate);
14	3-Phenyl-3-(2'-hydroxy-5'-chlorophenyl)-phthalide d	$C_{20}H_{13}ClO_3$ 336.5	C 71.0 H 3.9 Cl 10.5	C 71.4 H 4.1 Cl 10.7	89	240.6—242.1 from AcOH	1730s (C=O, γ -lactone), 1120s (OH, phenol), 975m (C—O—C, γ -lactone);
15	Methyl ether of phthalide d (da)	$C_{21}H_{15}ClO_3$ 350.5	C 71.9 H 4.3 Cl 10.1	C 71.8 H 4.7 Cl 9.8	90	157.8—158.4 from EtOH	2855w (CH ₃ , methyl ether), 1365w (CH ₃ , ether), 1255s (C—O—C, ether);
16	Acetate of phthalide d (db)	$C_{22}H_{15}ClO_4$ 378.5	C 69.8 H 4.0 Cl 9.4	C 70.2 H 4.4 Cl 9.8	86	159.3—160.6 from EtOH	1760s (C=O, acetate), 1380s (CH ₃ , acetate), 1195s (C—O—C, acetate);
17	2-(2'-Hydroxy-5'-chlorobenzhydryl)benzoic acid (dc)	$C_{20}H_{15}ClO_3$ 338.8	C 70.9 H 4.4 Cl 10.5	C 70.9 H 4.6 Cl 10.5	78	157.6—159.0 from EtOH	2780w (OH, dimer COOH), 1690s (C=O, COOH), 1170s (OH, phenol);
18	Acetate of acid dc (dd)	$C_{22}H_{17}ClO_4$ 380.8	C 69.4 H 4.5 Cl 9.4	C 69.5 H 4.7 Cl 9.2	85	165.8—167.1	1720s (C=O, acetate), 1380s (CH ₃ , acetate), 1220m (C—O—C, acetate);
19	ϵ -lactone of acid dc (df)	$C_{20}H_{13}ClO_2$ 320.5	C 74.9 H 4.1 Cl 11.1	C 74.6 H 4.0 Cl 11.0	83	202.1—203.1 from EtOH aq.	1720s (C=O, lactone), 1270s (C—O—C, lactone), 1040m (C—O, lactone);
20	3-Phenyl-3-(2'-hydroxy-5'-bromophenyl) phthalide (e)	$C_{20}H_{13}BrO_3$ 381.1	C 63.0 H 3.4 Br 21.0	C 63.1 H 3.4 Br 21.2	85	212.2—213.6 from AcOH ([14] 210—211)]	1740s (C=O, γ -lactone), 1115m (OH, phenol), 975m (C—O—C, γ -lactone);
21	Acetate of phthalide e (eb)	$C_{22}H_{15}BrO_4$ 423.1	C 62.4 H 3.5 Br 18.7	C 62.8 H 3.7 Br 18.4	87	149.6—151.0 from EtOH	1755s (C=O, acetate), 1375s (CH ₃ , acetate), 1200s (C—O—C, acetate);
22	2-(2'-Hydroxy-5'-bromobenzhydryl)benzoic acid (ec)	$C_{20}H_{13}BrO_3$ 383.1	C 62.7 H 3.9 Br 20.7	C 62.7 H 3.9 Br 20.5	82	116.8—118.3 from AcOH aq.	2720w (OH, dimer COOH), 1685s (C=O, COOH), 1190m (OH, phenol);
23	ϵ -lactone of acid ec (ef)	$C_{20}H_{13}BrO_2$ 364.9	C 65.8 H 3.6 Br 21.8	C 65.8 H 3.5 Br 21.9	92	227.4—229.5 from AcOH	1740s (C=O, lactone), 1265s (C—O—C, lactone), 1035m (C—O, lactone).

ε-lactones of 2-benzhydrylbenzoic acids dc and ec (df and ef)

To a solution of 2-benzhydrylbenzoic acid **dc** or **ec** (0.002 mole) in 15 cm³ Ac₂O 2 g anhydrous AcONa was added. The reaction mixture was heated for 3 h at 120 °C. This mixture was then poured into 300 cm³ of water. The crude precipitate yielded colourless crystals after recrystallization.

Reduction of phthalides b and e with Zn dust in 10% NaOH aq.

A sample of 0.005 mole of phthalide **b** or **e** was boiled with 5 g of Zn dust in a solution of 150 cm³ NaOH during 6 h. The mixture was filtered off and the filtrate was acidified with cc. HCl to pH 6. The crude, white precipitate was filtered off and washed with water. After recrystallizations from EtOH aq. colourless crystals of 2-(4'-hydroxybenzhydryl)benzoic acid from phthalide **b**, m.p. 208.6—210.2 °C ([15]: 210—211 °C), and 2-(2'-hydroxybenzhydryl) benzoic acid from phthalide **e**, m.p. 198.7—200.3 °C ([16]: 194—196 °C) were obtained.

9-Acetoxy-10-acetoxyhalogenophenyl)anthracenes (2, 3, 5, 7 and 8)

A mixture of 0.02 mole of the appropriate 2-benzhydrylbenzoic acid, 50 cm³ of Ac₂O and 1 drop of cc. H₂SO₄ was heated on an oil bath at 120 °C (in the case of the acid from 2-bromophenol at the b.p.) for 1—3 h until the TLC showed the absence of acid. The brown solution was then poured into 500 cm³ of water. The crude product was recrystallized several times from EtOH or AcOH yielding yellowish crystals of the halogen derivatives of 9-acetoxy-10-phenylanthracene. For results cf. Table II.

After heating in HNO₃/AcOH according to the described method [8], compounds **2**, **3**, **5**, **7**, and **8** gave anthraquinone in each case. Attempts to obtain the analogous derivative of anthracene from 3-bromophenol did not give positive results.

Measurement of electronic absorption and emission spectra

The absorption and emission spectra of the investigated compounds were recorded in 96% ethanol aq. at a concentration of $5.00 \cdot 10^{-5}$ mol/dm³. All compounds were recrystallized from EtOH and their purity was checked chromatographically (TLC) before use.

The electronic absorption spectra were recorded with a Zeiss VSU-2 spectrophotometer. The positions of the vibration peaks and the molar extinction coefficient values are listed in Table III.

Since the halogen atoms substituted in the phenyl ring of the investigated molecules cause only minor changes in the positions and the corresponding values of the extinction coefficients in Fig. 1 only the absorption spectra of 9-acetoxy-10-(4'-acetoxy-3'-chlorophenyl)anthracene (**2**), 9-acetoxy-10-(4'-acetoxy-2'-chlorophenyl)anthracene (**5**) and 9-acetoxy-10-(2'-acetoxy-5'-chlorophenyl)anthracene (**7**) are presented.

Table II

Data (elemental analyses, yields, m.p.'s, PMR and IR spectra) of new anthracenes (2, 3, 5, 7 and 8)

Compound	Formula, molecular mass	Analyses, %		Yield %	M.p. °C	PMR spectra δ ppm	IR spectra ν cm ⁻¹
		Calc.	Found				
2	C ₂₄ H ₁₇ ClO ₄ 404.9	C 71.2 H 4.2 Cl 8.8	C 71.3 H 4.2 Cl 8.8	68	169.8—171.3 from EtOH	2.32 (s, 3; 4'-OCOCH ₃), 2.56 (s, 3; 9-OCOCH ₃);	1760sb (C=O, acetate), 1370s (CH ₃ , acetate), 1220s (C—O—C, acetate);
3	C ₂₄ H ₁₇ BrO ₄ 449.3	C 64.2 H 3.8 Br 17.8	C 64.3 H 4.1 Br 17.7	57	181.8—183.0 from EtOH	2.33 (s, 3; 4'-OCOCH ₃), 2.56 (s, 3; 9-OCOCH ₃);	1780s (C=O, acetate), 1360s (CH ₃ , acetate), 1200s (C—O—C, acetate);
5	C ₂₄ H ₁₇ ClO ₄ 404.9	C 71.2 H 4.2 Cl 8.8	C 71.6 H 4.5 Cl 9.0	72	155.1—157.0 from EtOH	2.25 (s, 3; 4'-OCOCH ₃), 2.55 (s, 3; 9-OCOCH ₃);	1750s (C=O, acetate), 1370s (CH ₃ , acetate), 1240s (C—O—C, acetate);
7	C ₂₄ H ₁₇ ClO ₄ 404.9	C 71.2 H 4.2 Cl 8.8	C 71.4 H 4.4 Cl 8.8	84	159.8—161.0 from EtOH	1.43 (s, 3; 4'-OCOCH ₃), 2.55 (s, 3; 9-OCOCH ₃);	1755s (C=O, acetate), 1370s (CH ₃ , acetate), 1200s (C—O—C, acetate);
8	C ₂₄ H ₁₇ BrO ₄ 449.3	C 64.2 H 3.8 Br 17.8	C 64.3 H 3.9 Br 17.9	85	162.8—163.9 from AcOH	1.38 (s, 3; 4'-OCOCH ₃), 2.63 (s, 3; 9-OCOCH ₃);	1780s (C=O, acetate), 1370s (CH ₃ , acetate), 1200s (C—O—C, acetate).

Table III

Positions of the absorption and emission maxima of
9-acetoxy-10-arylanthracenes 1–10 in 96% EtOH aq.

Com- pound	Transition	Oscillator strength	Positions of the spectral peaks				
			Absorption			Emission	
			$\epsilon \frac{\text{dm}^2}{\text{mol}\cdot\text{cm}}$	$\epsilon/\epsilon_{\text{max}}$	ν_{abs} (cm ⁻¹)	I/I_{max}	ν_{f1} (cm ⁻¹)
1	2	3	4	5	6	7	8
1	$^1A \rightleftharpoons ^1L_a$	0.208	10 600	0.94	25 500	1.00	24 850
			11 300	1.00	26 900	0.97	23 700
			6 600	0.58	28 300	0.51	22 500
			3 500	0.31	29 800	0.16	21 000
			1 500	0.14	31 000		
	$^1A \rightarrow ^1B_b$	2.192	140 000		38 950		
$^1A \rightarrow ^1C_b$			77 500		40 200		
			19 000		44 850		
			20 000		46 000		
2	$^1A \rightleftharpoons ^1L_a$	0.249	13 350	0.95	25 400	0.88	25 150
			14 000	1.00	26 750	1.00	23 900
			8 900	0.64	28 250	0.47	22 550
			4 000	0.29	29 800	0.15	21 100
			1 150	0.08	31 100		
	$^1A \rightarrow ^1B_b$	1.984	116 650		38 950		
$^1A \rightarrow ^1C_b$			75 000		40 250		
			26 000		44 600		
			30 000		46 050		
3	$^1A \rightleftharpoons ^1L_a$	0.271	13 650	0.92	25 500	1.00	24 850
			14 850	1.00	26 800	1.00	23 700
			9 550	0.64	28 250	0.52	22 450
			4 300	0.29	29 750	0.17	20 900
			1 700	0.11	31 000		
	$^1A \rightarrow ^1B_b$	1.758	102 100		39 050		
$^1A \rightarrow ^1C_b$			71 600		40 150		
			21 500		44 600		
			24 600		46 300		
4	$^1A \rightleftharpoons ^1L_a$	0.243	13 050	0.93	25 450	0.97	24 850
			14 000	1.00	26 900	1.00	23 700
			8 950	0.64	28 400	0.51	22 600
			4 500	0.32	29 750	0.17	21 100
			1 850	0.13	31 000		
	$^1A \rightarrow ^1B_b$	2.498	173 350		39 000		
$^1A \rightarrow ^1C_b$			86 650		40 350		
			24 600		44 800		
			25 850		46 050		
5	$^1A \rightleftharpoons ^1L_a$	0.249	13 900	0.96	25 400	1.00	24 800
			14 500	1.00	26 900	1.00	23 750
			9 000	0.62	28 300	0.53	22 600
			3 900	0.27	29 800	0.20	21 100
			1 250	0.09	31 100		
	$^1A \rightarrow ^1B_b$	2.498	175 000		39 000		
$^1A \rightarrow ^1C_b$			93 300		40 400		
			28 000		44 600		
			31 250		45 900		

Table III

Compound	Transition	Oscillator strength	Positions of the spectral peaks				
			Absorption			Emission	
			$\epsilon \frac{\text{dm}^3}{\text{mol}\cdot\text{cm}}$	$\epsilon/\epsilon_{\text{max}}$	$\nu_{\text{abs}} (\text{cm}^{-1})$	I/I_{max}	$\nu_{j1} (\text{cm}^{-1})$
1	2	3	4	5	6	7	8
6	${}^1A \Rightarrow {}^1L_a$	0.209	11 000	0.93	25 500	0.97	25 000
			11 800	1.00	26 850	1.00	23 850
			7 500	0.64	28 350	0.50	22 550
			3 400	0.29	29 800	0.17	21 100
			1 350	0.11	31 000		
	${}^1A \rightarrow {}^1B_b$	2.217	153 350		38 950		
			81 750		40 200		
	${}^1A \rightarrow {}^1C_b$		18 350		46 200		
			18 800		47 800		
7	${}^1A \Rightarrow {}^1L_a$	0.257	13 400	0.95	25 500	0.96	24 950
			14 150	1.00	26 800	1.00	23 800
			9 200	0.65	28 300	0.50	22 500
			4 200	0.30	29 750	0.18	21 050
			1 600	0.11	31 100		
	${}^1A \rightarrow {}^1B_b$	2.187	134 100		39 000		
			85 500		40 100		
	${}^1A \rightarrow {}^1C_b$		29 100		44 900		
			29 200		45 900		
8	${}^1A \Rightarrow {}^1L_a$	0.252	13 150	0.95	25 500	0.97	24 900
			13 800	1.00	26 900	1.00	23 750
			9 000	0.65	28 300	0.51	22 600
			4 000	0.29	29 750	0.18	21 000
			1 500	0.11	31 100		
	${}^1A \rightarrow {}^1B_b$	2.004	116 650		39 050		
			75 100		40 200		
	${}^1A \rightarrow {}^1C_b$		29 150		44 800		
			29 100		45 800		
9	${}^1A \Rightarrow {}^1L_a$	0.222	11 900	0.93	25 500	1.00	24 850
			12 800	1.00	26 900	0.81	23 800
			7 900	0.62	28 300	0.31	22 200
			3 500	0.27	29 750	0.12	20 600
			1 600	0.13	31 200		
	${}^1A \rightarrow {}^1B_b$	2.803	202 000		38 850		
			124 500		40 350		
	${}^1A \rightarrow {}^1C_b$		37 000		44 800		
			30 500		46 000		
10	${}^1A \Rightarrow {}^1L_a$	0.222	11 650	0.94	25 500	1.00	25 000
			12 400	1.00	26 950	0.86	23 800
			8 000	0.64	28 400	0.41	22 400
			4 050	0.33	29 800	0.10	20 600
			1 950	0.16	31 200		
	${}^1A \rightarrow {}^1B_b$	2.525	185 000		38 900		
			95 000		40 350		
	${}^1A \rightarrow {}^1C_b$		24 500		44 900		
			28 000		46 500		

The fluorescence spectra of all compounds mentioned in the introduction were obtained using the apparatus described in [2]. The excitation of solutions was performed with an HBO-100 Hg lamp. The light beam passed through the monochromatic filter with $\lambda_{\max} = 365$ nm and half-width $\Delta\nu_{1/2} = 7$ nm. The luminophore was inducted perpendicularly to the observation direction. The fluorescent light emitted by the investigated solution was focused with a lens onto the slit of the SPM-2 monochromator. After passing the monochromator, the light fell on the cathode of the M12fQS-35 photomultiplier. Fluorescence of the beam leaving the monochromator had 1 nm half-width. The photocurrent of the photomultiplier was recorded with the G1B1 recorder. In Fig. 2 the intensities of the fluorescence spectra of these same compounds are shown. Here the sensitivity of the dispersion of photomultiplier and the prism were taken into account. Table III gives more definite data on the absorption and emission spectral of all the investigated compounds.

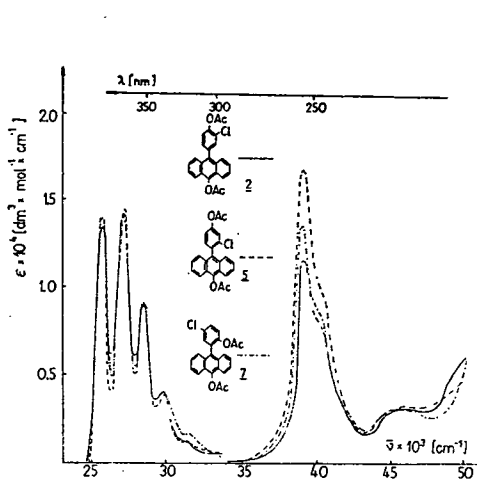


Fig. 1. Electronic absorption spectra in 96% ethanol

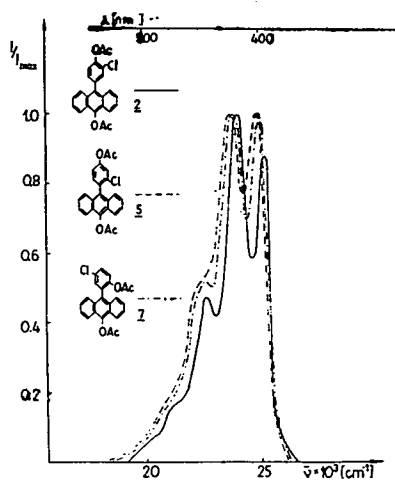


Fig. 2. Emission spectra in 96% ethanol

Results and discussion

As mentioned earlier, auxochromes substituted in the phenyl ring of the investigated molecules exert less influence on the absorption and emission spectra than in the case of their substitution in the anthracene skeleton. For the purpose of illustration of the changes of extinction coefficients caused by halogen substitution in the phenyl ring, the oscillator strength was calculated for the first two electronic transitions using eqn. (1):

$$f = \frac{3mcn}{e^2} \int \epsilon_{\nu\mu} d\nu. \quad (1)$$

In eqn. (1) n is the refractive index, m and e are the mass and charge of the electron, and c is the velocity of light. The values of the absorption integral were calculated

using the data of the measured absorption spectrum. The oscillator strength values for the first two electronic transitions of the respective compounds are also given in Table III.

From the analysis of the positions of the first two bands and the oscillator strength values it can be concluded that:

- The introduction of halogen atoms into position 3' of 9-acetoxy-10-(4'-acetoxyphenyl)anthracene (9) causes no change in the position of the ${}^1A \rightleftharpoons {}^1L_a$ band (except for molecule 1), but a slight bathochromic shift) (100 cm^{-1}) of the ${}^1A \rightarrow {}^1B_b$ band.
- The introduction of halogen atoms into position 2' of molecule 9 causes a bathochromic shift of the ${}^1A \rightleftharpoons {}^1L_a$ band and a hypsochromic shift of the ${}^1A \rightarrow {}^1B_b$ band. These effects depend on the atomic weight of the halogen atom.
- The substitution of halogens into position 5' of 9-acetoxy-10-(2'-acetoxyphenyl)anthracene (10) causes no change in the position of the ${}^1A \rightleftharpoons {}^1L_a$ band, but the ${}^1A \rightarrow {}^1B_b$ band is regularly shifted hypsochromically by 50, 100 and 150 cm^{-1} for F, Cl and Br, respectively.

The calculated oscillatory strength, which is proportional to the transition probability of the given absorption band, suggests that halogens substituted into position 3' or 2' of 9-acetoxy-10-(4'-acetoxyphenyl)anthracene (9), or into position 5' of 9-acetoxy-10-(2'-acetoxyphenyl)anthracene (10) causes an increase of ca. 14% in its value. An exception is observed for the molecules substituted with fluorine, where f is smaller than for the unsubstituted molecules. It must be noted that the intensity of the ${}^1A \rightarrow {}^1B_b$ band is smaller for all molecules with the substituted halogen. The f value of the ${}^1A \rightarrow {}^1B_b$ band for substituted molecules diminished on average by ca. 22% for halogen derivatives of compound 9 and by ca. 16% for halogen compounds of compound 10. It should be pointed out that smaller changes of intensity of this band are observed for F-substituted than for Br-substituted compounds. The changes of f values in the intensities are proportional to the atomic weight of the halogen.

The half-widths of the long-wave absorption bands for the halogen derivatives of compounds 9 and 10 are smaller than those for the unsubstituted molecules. This difference is about 100 cm^{-1} and differs slightly for the various molecules. It should be noted that the half-width of the long-wave absorption band is about 500 cm^{-1} greater than that in the fluorescence spectrum. As BERLMANN [17] has suggested in his detailed paper, the above dependence may be explained by the weaker influence of the phenyl substituent with the anthracene skeleton in the excited state 1L_a than in the ground state 1A . This appears when the angle between the planes of the benzene ring and the anthracene skeleton in the investigated molecules is greater in the excited state 1L_a than in the ground state 1A . Differences in interactions are also observed in the absence of the mirror symmetry of the electronic absorption and emission spectra, as well as differences of the ring-localized vibrational modes of the anthracene skeleton.

The above finding is corroborated by the spectra of 9-acetoxy-10-(4'-acetoxy-2'-fluorophenyl)anthracene (4) and 9-acetoxy-10-(4'-acetoxy-2'-chlorophenyl)anthracene (5), in which three vibrational peaks are distinctly visible, formed due to the damping of the torsional vibrations of the phenyl ring.

The investigated derivatives of 9-acetoxy-10-phenylanthracene are non-ionized in ethanol medium. Solvates can form between the carbonyl group of the ester acid radical and the hydrogen atom of the hydroxy group of ethanol, and between a halo-

gen atom and the hydroxy group of ethanol. The above phenomenon causes an increase of the reflection index and an increase of the Stoke shift $\Delta\nu_s$, of ca. 500—600 cm^{-1} for the investigated compounds. The observed differences between the $\Delta\nu_s$ values of the respective molecules do not allow any relationships to be established.

We hope that our further experimental studies, e.g. on the quantum yield and mean lifetime of the fluorescence experimentally determined and calculated from the absorption spectra of these compounds, will give valuable information on the structure. These measurements will also contribute data on the influence of the halogen substituents and other auxochromes on the spectroscopic parameters, e.g. the quantum yield, mean lifetime and gain coefficient of stimulated emission.

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ПРОИЗВОДНЫЕ 9-АЦЕТОКСИАНТРАЦЕНОВ. ЧАСТЬ IX. СИНТЕЗЫ И СПЕКТРАЛЬНОЕ ИЗУЧЕНИЕ 9-АЦЕТОКСИ-10-(АЦЕТОКСИГАЛОГЕНОФЕНИЛ)-АНТРАЦЕНОВ

Й. Гроновска, А. Дзеленьджак и Й. Хельдт

Синтезированы некоторые 9-ацетокси-10-(ацетоксигалогенофенил)антрацены. Изучено влияние галогенных заместителей на электронные спектры поглощения и испускания, а также на силу осциллятора.