Influence of Internal Heavy Atoms on the Spectroscopic Properties of 9-Acetoxy-10-Phenylanthracene Derivatives

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Absorption and fluorescence spectra, fluorescence quantum yields and decay times have been measured for new derivatives of 9-acetoxy-10-acetoxyhalogenophenylanthracene in dioxane. It is found that the strength of the absorption transition decreases with increases atomic number Z of the halogen substituent whereas the strength of the fluorescence transition is constant with the exception for the fluoro-substituted derivatives. The loss of mirror symmetry between the absorption and fluorescence spectra is more evident for the 10-(4-acetoxy-3′-halogenophenyl)anthracene derivatives than for the remaining compounds. The determined nonradiative electronic relaxation rate constant and "dark reactions" quantum yield increases with increasing Z value. These findings are explained on the basis of the spin-orbit coupling enlarged by the heavy substituent and through perturbation of the functional groups, which causes different changes of the molecular geometries in the S_0 and S_1^* states, respectively.

Introduction

In numerous papers it has been shown that the presence of an internal [1–4] and external [5, 6] heavy atom enhances the spin-orbit interaction in the molecule causing changes in transition probabilities of several deexcitation channels. These changes affect the fluorescence and phosphorescence (α and β) intensities, the fluorescence decay time (τ_F) and the quantum yield (Q_F). Moreover in some cases, if the heavy atom is substituted on the main skeleton of the fluorescence molecule, the polarization spectra are changed also [2, 7]. The spectroscopic parameters of anthracene heavy atom derivatives are very sensitive to the position of substitution [8]. Most of the substituted molecules show small red shifts of the absorption and fluorescence spectra from that of the unsubstituted molecule.

The purpose of these studies is to show the influence of an internal heavy atom substituted in the phenyl ring of some derivatives of 9-acetoxy-10-phenylanthracene on the absorption and fluorescence spectra; fluorescence decay time and quantum yield and on the rate constant of nonradiative processes.

1. Experimental

1.1. Chemicals

The compounds are: 9-acetoxy-10-(4′-acetoxyphenyl)anthracene (I); 9-acetoxy-10-(4′-acetoxy-3′-fluorophenyl)anthracene (II); 9-acetoxy-10-(4′-acetoxy-3′-chlorophenyl)anthracene (III); 9-acetoxy-10-(4′-acetoxy-3′-bromophenyl)anthracene (IV); 9-acetoxy-10-(4′-acetoxy-2′-fluorophenyl)anthracene (V); 9-acetoxy-10-(4′-acetoxy-2′-chlorophenyl)anthracene (VI); 9-acetoxy-10-(2′-acetoxyphenyl)anthracene (VII); 9-acetoxy-10-(2′-acetoxy-5′-fluorophenyl)anthracene (VIII); 9-acetoxy-10-(2′-acetoxy-5′-chlorophenyl)anthracene (IX); and 9-acetoxy-10-(2′-acetoxy-5′-bromophenyl)anthracene (X).

The compounds were obtained and purified by Gronowska and co-workers (see [9]). The solvent dioxane was of spectral purity. In these studies the concentration of the compounds was 5×10^{-5} mol/l. All measurements were performed at room temperature with air saturated dioxane solutions.

1.2. Absorption and fluorescence spectra

The absorption spectra were measured with a Zeiss-Jena VSU type spectrophotometer. The emission spectra were recorded photoelectrically using a grating monochromator and M12FQS35 photomultiplier connected to the X-t recorder. The molecules

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were excited by radiation from a high-pressure Xenon lamp through a monochromatfilter ($\lambda_{\text{trans}} = 363$ nm; $\Delta\lambda_{1/2} = 5.5$ nm). The fluorescence spectra were recorded in the frontally illuminated setup where the fluorescence light was observed at a small angle to the excitation beam. The emission spectra are corrected for the spectral response of the detecting system.

1.3. *Fluorescence decay time determination*

The fluorescence decay time measurements were performed by means of the phase-modulated fluorometer constructed by Bauer et al. [10]. As a reference fluorophor a sample of dimethyl POPOP in ethanol was used. The relative phase angle $\Delta\varphi$ of the output signal from the anode LC-circuits of both photomultipliers (measuring the reference and fluorescence light) is measured by means of a digital phasemeter. The decay time is calculated as $\tau_{\text{exp}} = \text{tang}\, \Delta\varphi / 2\pi\nu$, where ν is the modulation frequency. The decay time of the solution was measured several times independently and the results were averaged. They are collected in column 5 of Table 1 (upper number). The estimated error of the absolute τ_{exp} value equals to ± 0.1 ns.

1.4. *Determination of the fluoresence quantum yield*

The fluorescence quantum yields were determined by means of a photoelectric method described in the paper of Kawski et al. [11]. The apparatus was calibrated using as the standard a solution of 9,10-diphenylanthracene in dioxane for which the quantum yield is 0.83 according to Ref. [12]. This value was prefered to the value 0.73 following from Ref. [12a]. The quantum yield was then calculated from the expression

$$Q_{\mathrm{F}} = Q_{\mathrm{F}}^{\mathrm{R}} \frac{\int_0^\infty I_{\mathrm{F}}(\nu)\, \mathrm{d}\nu}{\int_0^\infty I_{\mathrm{F}}^{\mathrm{R}}(\nu)\, \mathrm{d}\nu} \, \frac{\varepsilon^{\mathrm{R}}(\nu)}{\varepsilon(\nu)} \left(\frac{n}{n^{\mathrm{R}}}\right)^2 , \tag{1}$$

where $I_{\mathrm{F}}(\nu)$, $I_{\mathrm{F}}^{\mathrm{R}}(\nu)$ and $\varepsilon(\nu)$, $\varepsilon^{\mathrm{R}}(\nu)$ are the fluorescence intensities and molar extinction coefficients of the measured sample and the standard (R), respectively. n and n^{R} are the refractive indexes of the solvents. The quantum yield was measured five times independently. The average values of Q_{F} are placed in column 6 of Table 1. The experimental error is estimated to be ± 0.05.

2. Results and Discussion

2.1. *Absorption and emission spectra*

Halogen atom substituted ion in organic dyes shifts the absorption and fluorescence spectra and changes progressively the intensities. In the case of the studied compounds the absorption and fluorescence spectra are somewhat red shifted (see Figs. 1 and 2). They show in absorption a distinct structure with five anthracene ring-localized vibrational modes. The frequency differences between neighbouring vibrational peaks are constant (within the error limits of their determination) and equal to those of the parent molecule. The fluorescence spectra (see Figs. 1 and 2) do not perform exactly the so-called mirror symmetry, the differences show up in a blurred vibrational structure and in weakly distinct four vibrational modes only. The fluorescence spectra of compounds possessing the − OAc group or a halogen atom in position 2′ of the phenyl ring show better marked vibrational structure. The frequency difference between neighbouring vibrational peaks of the fluorescence spectrum differ from those in absorption.

It follows from Figs. 1 and 2 that introduction of the halogen atom into the phenyl ring causes slight intensity changes of the absorption spectra. The extinction coefficients, $\varepsilon_{\max}$, (see Table 1, column 3) possess generally bigger values. An exception is observed for the molecules III, V and VII. The changes of $\varepsilon_{\max}$ and $\int \varepsilon(\nu)\, d \ln \nu$ (see Table 1) show no regularities.

Analyzing the spectra more exactly it can be noticed that the width of the absorption, FWRE(A), and emission, FWRE(F), spectra determined at reciprocal "e" of the maximum value of $\varepsilon(\nu)$ and $I_{\mathrm{F}}(\nu)$ differ by about 300 cm^{-1} and vary for various molecules (see Table 1, column 8). The absence of mirror symmetry and the smaller values of the fluorescence spectra widths (FWRE(A) > FWRE(F)) suggest that the phenyl substituent weakly interact with the anthracene skeleton in the ground state ^{1}A than in the first excited state $^1\mathrm{L}_{\mathrm{a}}$. This appears when, in the molecules under study, the angle between the planes of the phenyl ring and the anthracene skeleton is bigger in the excited state than in the ground state [13].

According to Berlman [13, 14] more reliable data, which could confirm this statement and give some information concerning the nuclear topology of the

Table 1. The fluorescence decay time τ_{exp}, quantum yield Q_F, and maximum extinction coefficient $\varepsilon_{\mathrm{max}}$. The calculated values of the center of gravity of the absorption, ν_A^{cg}, and fluorescence, ν_F^{cg}, spectra, the Stokes shift ν_{ST} and the fluorescence, k_F, and "dark process", k_D rate constants are given also.

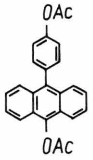
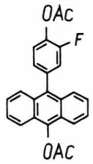
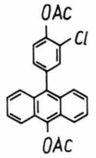
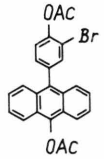
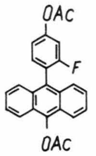
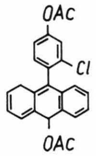
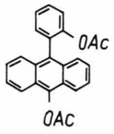
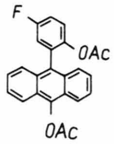
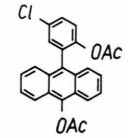
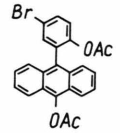
No.	Molecule	$\varepsilon_{\mathrm{max}}$ $[1\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}]$ $\int \varepsilon(\nu)\, d\ln\nu$	$\left.\begin{matrix}\nu_A^{cg}\\ \nu_F^{cg}\\ \nu_{ST}\end{matrix}\right\}$ $[\mathrm{cm}^{-1}]$	$\left.\begin{matrix}\tau_{\mathrm{exp}}\\ \tau_A^0\\ \tau_F^0\end{matrix}\right\}$ [ns]	Q_F Q_D	$\left.\begin{matrix}k_F\\ k_D\end{matrix}\right\}\times 10^7\ [\mathrm{s}^{-1}]$	FWRE(A) FWRE(F) in $[\mathrm{cm}^{-1}]$
1	2	3	4	5	6	7	8
I		11 800 1 314	27 056 23 640 1 708	8.88 10.17 9.26	0.96 0.04	10.80 0.45	3 900 3 600
II		12 800 1 455	27 298 23 196 2 051	9.06 9.10 10.65	0.85 0.15	9.38 1.66	4 000 3 650
III		11 500 1 329	27 440 23 410 2 000	8.81 10.28 11.29	0.78 0.22	8.85 2.50	3 900 3 650
IV		12 250 1 416	27 272 23 377 1 947	7.96 9.72 10.21	0.73 0.27	9.17 3.39	3 900 3 700
V		10 700 1 208	27 380 23 499 1 940	8.84 11.17 11.79	0.75 0.25	8.48 2.83	3 850 3 500
VI		12 300 1 278	27 610 23 627 1 992	8.74 10.42 11.97	0.73 0.27	8.35 3.9	3 750 3 500
VII		11 300 1 248	27 286 23 604 1 841	9.33 10.96 9.93	0.94 0.06	10.11 0.65	3 850 3 650
VIII		11 100 1 185	27 424 23 592 1 916	9.14 11.34 11.28	0.82 0.18	8.97 1.97	3 900 3 600

Table 1. (continued)

No.	Molecule	ε_{max} [l mol^{-1} cm^{-1}] $\int \varepsilon(\nu)\, d \ln \nu$	ν_A^{cg} ν_F^{cg} ν_{ST} [cm^{-1}]	τ_{exp} τ_A^0 τ_F^0 [ns]	Q_F Q_D	k_F k_D × 10^7 [s^{-1}]	FWRE (A) FWRE (F) in [cm^{-1}]
1	2	3	4	5	6	7	8
IX		12200 1355	27400 23487 1957	9.12 10.04 11.40	0.80 0.20	8.88 2.14	3900 3600
X		12000 1348	27349 23540 1905	8.58 10.02 11.29	0.76 0.24	8.85 2.80	3850 3600

ground and excited states, comes from calculations of the natural radiative lifetime of the long-wave electronic transition and from the Stokes shift. The natural radiative lifetimes have been determined from the absorption and fluorescence curves by use of the Strikler-Berg formula [15]

$$(\tau_A^0)^{-1} = 2.88 \cdot 10^{-9}\, n^2 \,\frac{\int I_F(\nu)\, \mathrm{d}\nu}{\int \nu^{-3} I_F(\nu)\, \mathrm{d}\nu} \int \varepsilon(\nu)\, d \ln \nu, \quad (2)$$

where n is the refractive index of the medium and $I_F(\nu)$ the fluorescence intensity, and from the inverse of the fluorescence rate constant, k_F, which is equal to

$$\tau_F^0 = \tau_{exp}/Q_F. \quad (3)$$

The labels A and F (in (2) and (3)) indicate the use of absorption and fluorescence data in determination the natural radiative lifetime τ^0. The integrals

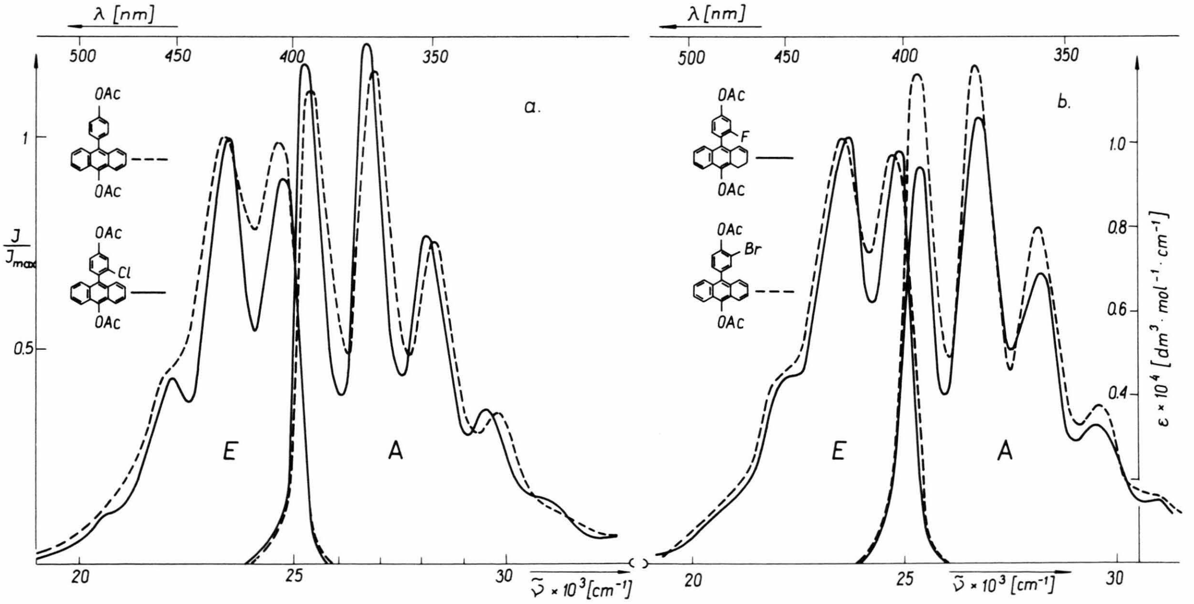


Fig. 1. Absorption and fluorescence spectra of: a (9-acetoxy-10-(4′-acetoxyphenyl)anthracene (I, – – –), 9-acetoxy-10-(4′-acetoxy-2′-chlorophenyl)anthracene (VI,——); b (9-acetoxy-10-(4′-acetoxy-2′-fluorophenyl)anthracene (V, ——), 9-acetoxy-10-(4′-acetoxy-3′-bromophenyl)anthracene (IV, – – –) in dioxane.

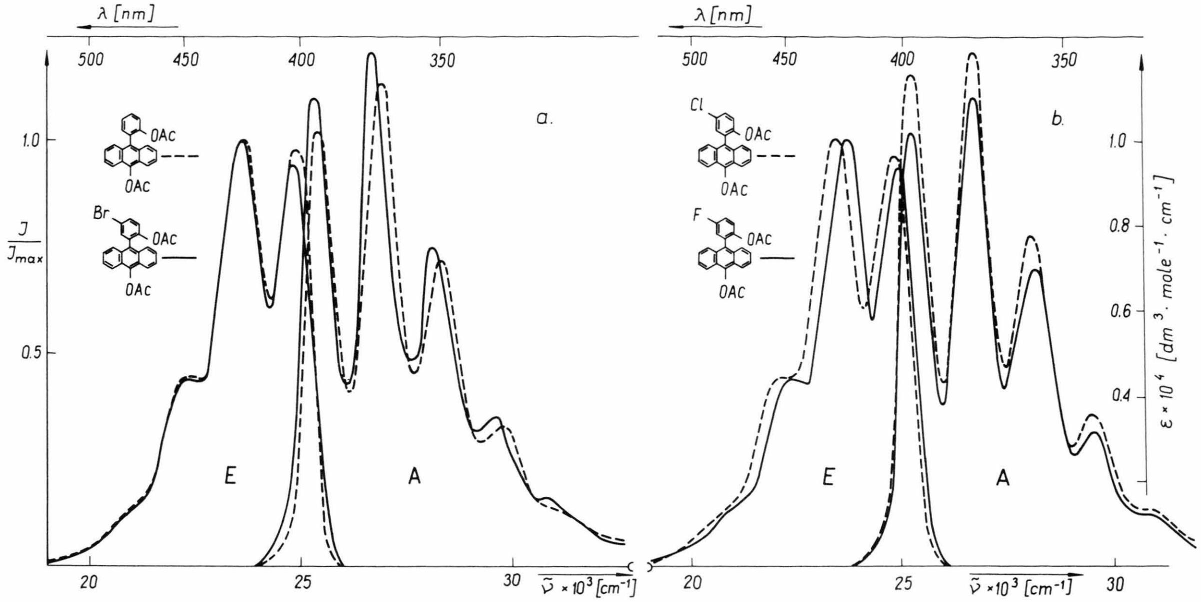


Fig. 2. Absorption and fluorescence spectra of: a) 9-acetoxy-10-(2′-acetoxyphenyl)anthracene (VII, – – –), 9-acetoxy-10-(2′-acetoxy-5′-bromophenyl)anthracene (X, —); b) 9-acetoxy-10-(2′-acetoxy-5′-chlorophenyl)anthracene (IX, – – –), 9-acetoxy-10-(2′-acetoxy-5′-fluorophenyl)anthracene (VIII, —) in dioxane.

appearing in (1) and (2) were determined from our measurements using the method of Simpson [16]. Calculating τ_A^0, we used the n value of pure solvent, for dioxane 1.42. The computed values of τ_A^0 and τ_F^0 are collected in column 5 (lower numbers) of Table 1. An analysis of the results reveals that for the halogen derivatives of 9-acetoxy-10-(4′-acetoxyphenyl)anthracene (I) or 9-acetoxy-10-(2′-acetoxyphenyl)anthracene $\tau_F^0 > \tau_A^0$, with an exception for compound VIII. The parent molecules show a distinctly opposite dependence. The differences between τ_F^0 and τ_A^0 are of the order 1.2 ns on the average; it constitute a value bigger than the estimated error.

Since the absorption and fluorescence spectra do not perform exactly the mirror image similarity we determined the Stokes shift using the formula:

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

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

$$\nu_A^{cg} = \int \nu\, \varepsilon(\nu)\, d\nu / \int \varepsilon(\nu)\, d\nu,$$

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

The integrals appearing in (5) are determined in the same way as in (2). In Table 1, column 4 are collected the values of ν_A^{cg}; ν_F^{cg} and ν_{ST}. Figure 3 shows graphically the dependence of ν_A^{cg} and ν_F^{cg} on the atomic number Z of the halogen substituent. The dependence of ν_A^{cg} and ν_F^{cg} on Z is linear (see Figure 3). The frequencies ν_A^{cg} of the studied compounds dissolved in dioxane increase with increasing atomic number Z of the halogen substituent. The frequency ν_F^{cg} shows an opposite dependence. Analyzing the Stokes shift frequencies it results that the halogen substituted compounds possess larger ν_{ST} values than the parent molecules (about 250 cm^{-1} on the average).

The big increase of ν_{ST} of the halogeno-derivatives of the compounds I and VII can be explained by inter- and intramolecular interactions which are different for the substituted and parent molecules.

2.2. *Fluorescence decay time and quantum yield*

The luminescence properties of the compounds under study are influenced by two factors: the substituted halogen atom and interaction with environmental molecules. The internal heavy atom can

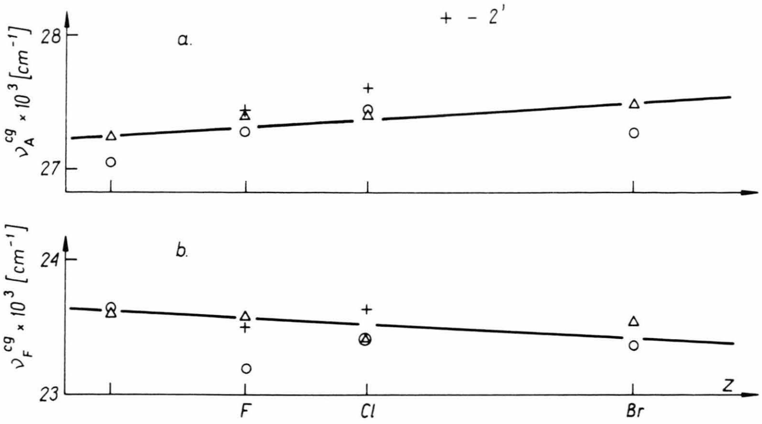


Fig. 3. The ν_A^{cg}, ν_F^{cg} and ν_{ST} values vs. the atomic number Z. The points marked by "○" and "△" correspond to the derivatives of compound I and VII, respectively. Compounds V and VI are marked by crosses.

enhance the radiative and nonradiative electronic relaxation probabilities. The relevant photophysical relaxation processes of particular interest are:

$$\begin{aligned} A + h\,\nu_{ab} &\longrightarrow A^* && \text{– absorption,}\\ A^* &\xrightarrow{k_F} A + h\,\nu_F && \text{– fluorescence,}\\ &\xrightarrow{k_{IC}} A && \text{– internal conversion,}\\ &\xrightarrow{k_{ISC}} {}^3A && \text{– intersystem crossing.} \end{aligned}$$

The luminescence quantities, determined in the measurements performed by us, are related with the above rate constants in following way:

The fluorescence quantum yield

$$Q_F = k_F/(k_F + k_{IC} + k_{ISC})\,, \tag{6}$$

the fluorescence decay time

$$\tau_{exp} = 1/(k_F + k_{IC} + k_{ISC})\,. \tag{7}$$

It follows from (2) and (3) that

$$k_D \equiv k_{IC} + k_{ISC} = \tau_{exp}^{-1} - k_F\,, \tag{8}$$

where the fluorescence rate constant $k_F = Q_F/\tau_{exp}$.

The quantum yield of nonradative processes "dark reactions" is given by the equation

$$Q_D = k_D/(k_F + k_D)\,. \tag{9}$$

In columns 5 and 6 (upper numbers) of Table 1 are collected the values of the fluorescence decay times and quantum yields as well as the calculated rate constants k_F and k_D. The above quantities, determined for the compounds under study, show a dependence on the Z-value of the halogen atom. Figure 4 shows the ratios of the fluorescence decay times and quantum yields of the halogen substituted molecules to the parent compounds vs. Z. It follows from Fig. 4 that the quantum yield of the halogen derivatives decreases more rapidly with

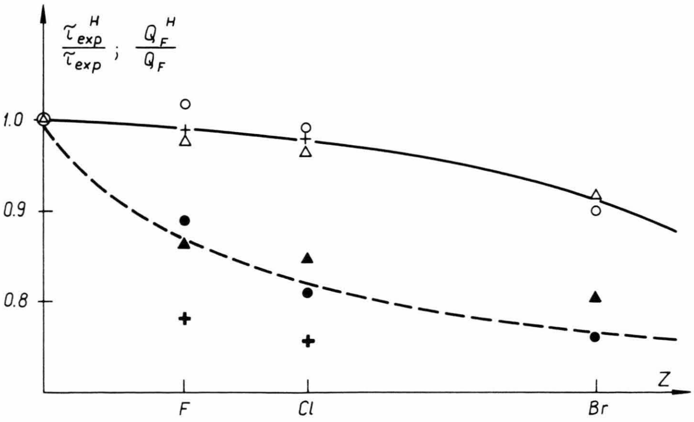


Fig. 4. The ratios of τ_{exp}^H/τ_{exp} and Q_F^H/Q_F versus Z. The full points, triangles and heavy crosses assign the ratio of Q_F^H/Q_F. The index "H" indicates the halogeno derivatives. The points are labeled as in Fig. 3.

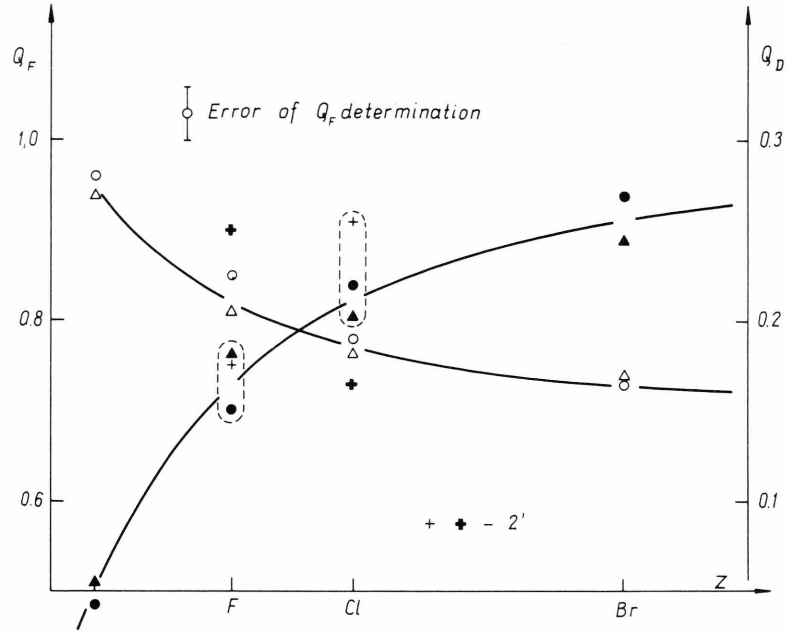
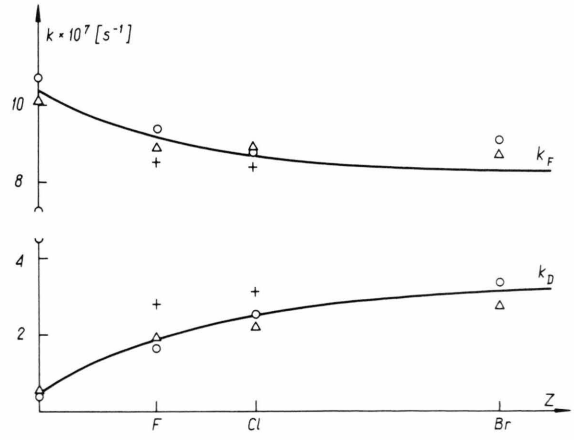


Fig. 5. The quantum yield of fluorescence and nonradiative processes vs. Z. The points are labeled as in Figure 3.

increasing Z than the fluorescence decay times. This indicates an appearance of nonradative processes in the studied compounds.

Figures 5 and 6 illustrate graphically the Q_F, Q_D and k_F, k_D dependence on the Z-value of the substituted atom. An analysis of the results reveals that the fluorescence quantum yield Q_F and the rate constant k_F decrease with increasing atomic number Z of the halogen atom. The inverse dependence is found for the "dark reactions" rate constant k_D and quantum yield Q_D.



On the base of many papers [8, 17–19] the observed changes of the k_F, Q_F and k_D, Q_D values with increasing atomic number Z can be explained through the spin-orbit coupling of the π-electrons in the anthracene skeleton enlarged by the heavy substituent. Small deviations from the curves assigned by the majority of the experimental points are found for the compounds V and VI. This departure, as it has been suggested in [9], can be caused by hydrogen bonding between the halogen and hydrogen atoms of the phenyl and anthracene ring, respectively. It is interesting to notice (see Table 1 and Fig. 5) that the sum of k_F and k_D of the halogen substituted compounds is equal to the sum obtained for the parent molecules (I and VII) within the error limits.

Results of other authors [17–19] and our findings suggest that for the halogen derivatives of 9-acetoxy-10-phenyl anthracene the rate constant of intersystem crossing increases as the atomic number of the substituent halogen atom increases whereas the rate constant of internal conversion is constant.

3. Summary

The results obtained from our measurements and calculations show that:

1. The quantum yields of the derivatives of 9-acetoxy-10-phenylanthracene form halogenophenols are smaller than those of the parent compounds and vice versa for the quantum yield of non-radiative processes.
2. For the substituted compounds the natural radiative life times fulfill the dependence $\tau_F^0 > \tau_A^0$.
3. The studied halogen derivatives characterizes a large value of the extinction coefficient and Stokes shift. They are smaller for parent molecules. The mirror symmetry between the absorption and fluorescence spectra is not strictly preserved in the series of related compounds.

The above findings, according to Berlman's [13, 14] classification of ring and ring-chain systems, suggest that the studied compounds possess different nuclear conformation (planarity) in the ground ^1A and excited ^1L_a states. The noticed changes in Q_F, Q_D, k_F and k_D values are due to the spin-orbit coupling enlarged by the heavy substituent. All compounds show laser action if excited with light of the N_2-laser [20].

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