Spectroscopy and Photophysics of Monoazaphenanthrenes I. Absorption and Fluorescence Spectra of Phenanthridine and 7,8-Benzoquinoline

M. Norek, J. Dresner and J. Prochorow

Institute of Physics, Polish Academy of Sciences
al. Lotników 32/46, 02-668 Warsaw, Poland

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The absorption and fluorescence spectra of phenaentridine and 7,8-benzoquinoline have been measured in liquid solutions of non-polar, aprotic hydrocarbon solvents (*n*-hexane and cyclohexane) and in strongly polar (and hydrogen-bonding) methanol. The analysis of the Stokes' shift between absorption and fluorescence spectra has shown that for both molecules the observed solvent effects on their absorption and fluorescence spectra can be described in terms of universal solvent–solute interactions (no evidence of specific solvent–solute interactions, of the type of hydrogen bond formation with participation of lone-pair electrons of nitrogen atom, has been found). On the other hand, the measured decay time profiles of fluorescence are visibly longer in methanol solution than in non-polar, aprotic solvents and these observations are consistent with the observed increase in fluorescence intensity of both molecules in strongly polar methanol solution. The radiative lifetimes of the first excited singlet state do not differ noticeably for both molecules, but it has turned out that in the case of phenanthridine the nonradiative processes are getting less effective in methanol solution than in the case of 7,8-benzoquinoline, which can presumably be related to the role of different position of the substitution of nitrogen atom in these two molecules.

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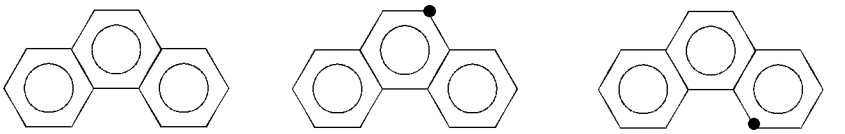
1. Introduction

The present work was stimulated by the results of our earlier studies of spectroscopy and photophysics of acridine. This molecule — monoaza-derivative of anthracene (with N atom substituted in a central ring of aromatic skeleton

of anthracene) — has been the subject of numerous studies since the mid of the last century [1–3]. For all practical purposes it does not fluoresce in aprotic, non-polar solvents (such as *n*-hexane) and exhibits fairly intense fluorescence in polar, hydrogen-bonding solvents (alcohols and water), and on the grounds of these observations acridine molecule served as a clear example of the inversion of excited $^1n\pi^*$ and $^1\pi\pi^*$ singlet states induced by hydrogen-bonding solvents [4]. The observations of laser induced fluorescence and fluorescence excitation spectra of acridine under molecular supersonic jet conditions (in helium jet) have univocally showed that acridine molecules do not fluoresce and that the observed fluorescence originates from acridine dimers, which are formed under such jet-cooling conditions [5, 6]. The acridine dimer ground-state geometry, determined by semi-empirical AM1 and PM3 parametric methods, is a head-to-tail-like structure with almost co-linear arrangement of short axis of both molecular components of the dimer and almost co-planar arrangement of their molecular planes. In such a structure (which is also stabilized by N $\cdots$ H–C hydrogen bond formed between two molecular components in the dimer) a large enhancement of the oscillator strength for the transition from the ground to first excited singlet state of the dimer is predicted by the calculations (though the lowest excited singlet, S_1, state of acridine molecule is found to be clearly of $\pi\pi^*$ character). Furthermore, the analysis of the rotational band contour for the origin transition of fluorescence excitation spectrum of acridine dimer has shown that there is a possibility of existence of slightly different conformations of the dimer [7].

The mechanism of the effective enhancement of radiative transition from the ground to excited state in acridine dimer is solely connected with its unique, highly symmetrical structure, governed to a large extent by the symmetry of acridine molecule itself. Such a mechanism could hardly be expected for other members of monoaza families of polycyclic aromatic hydrocarbons, which are lacking symmetry elements, due either to the lost of symmetry upon the substitution of N atom into the parent hydrocarbon (as in the case of other monoazaanthracenes), or to the lack of symmetry of the parent hydrocarbon molecule itself. First and natural example would be a nonlinearly condensed three-cyclic system of phenanthrene molecule and its monoaza-derivatives, such as phenanthridine and 7,8-benzoquinoline, of the structure shown below (with the black dot indicating the N atom position):



It seems that azaphenanthrenes are especially good candidates for verification of such expectations, as they have no symmetry elements and the degree of exposure of their lone-pair n-orbitals to intermolecular specific interactions (such as hydrogen bond formation) is different for different azaphenanthrenes (a different position of N atom in the aromatic ring system of phenanthrene, as shown above). Since a long time, such monoazaphenanthrenes as phenanthridine, 5,6-benzoquinoline, and 7,8-benzoquinoline, were known to undergo, under appropriate pH conditions of solvents, the excited-state protonation reaction, due to the increase of their basicity upon excitation [8–10]. Studies of the fluorescence spectra of these molecules (and their conjugated acid forms) in basic and acidic aqueous solutions [11] clearly demonstrated that their fluorescence is fairly efficient and is characterized by the lifetimes of nanoseconds (and by the radiative and nonradiative rate constants of comparable magnitudes). Thus, the lowest excited singlet state of this monoazaphenanthrenes is of $\pi\pi^*$ character (equivalent to ^1L_b, $^1\pi\pi^*$ state of phenanthrene), contrary to general, though oversimplified expectation, that the substitution of N atom into the condensed-ring-skeleton system of polycyclic hydrocarbon must lead to the lowest excited singlet state of the molecule of $n\pi^*$ character ($n \rightarrow \pi^*$ transition), due to the introduction of lone-pair electrons (non-bonding electrons on the nitrogen atom). However, the arguments based on higher energy of n electrons than the energy of the highest filled π orbital, which might be in general true for carbonyl substituted polyenes, do not necessarily hold in the case of aza-substituted polycyclic hydrocarbons. In this family, other parameters, such as distortion of angular symmetry of ring-skeleton, hydrogen bonding and/or protonation in the excited state with solvents molecules, and presumably a balance between conjugative and inductive effects of substituents, must also be taken into account in the characterization and relative ordering of the $n\pi^*$ and $\pi\pi^*$ excited singlet states [12].

In this report we present the results of comparative investigations of absorption and fluorescence spectra of phenanthridine (PHN) and 7,8-benzoquinoline (BQ) in non-polar, aprotic hydrocarbon solvents (n-hexane and cyclohexane) and in polar, hydrogen-bonding methanol. The effects of solvents on the spectra are compared with spectra of parent phenanthrene (PH) and together with the results of studies of the solvent effects on photophysical parameters (the decay times of fluorescence and the rates of radiative and nonradiative processes) should form the grounds for theoretical description of the effects of the N atom substitution and its position in PH skeleton, on molecular and spectral parameters in monoazaphenanthrenes under consideration.

2. Experimental procedures

Phenanthridine (purum for fluorescence) and 7,8-benzoquinoline (purum 99% (NT)) were obtained from Fluka and were recrystalized from 1:9 ethanol/water

mixture and after this preliminary purification they were sublimed *in vacuo* prior to the use. Phenenthrene from Aldrich Chemical Co. was purified by multipass zone-refining. Solvents from Merck, *n*-hexane and cyclohexane (both pure for spectroscopy) and methanol (for UV spectroscopy), were used without further purification (after checking the lack of the fluorescence background in the investigated spectral region).

Absorption spectra were collected with the use of UV-3100 Shimadzu Recording Spectrophotometer (courtesy of Photochemistry and Spectroscopy Laboratory at the Institute of Physical Chemistry of Polish Academy of Sciences, Warsaw). Cuvettes of different path lengths (from 1.0 to 0.1 cm) were used at different spectral regions and/or for different samples' concentrations.

For measurements of fluorescence spectra, the home-computerized Perkin–Elmer 512 spectrofluorimeter was used. In measurements of fluorescence decays, fluorescence was excited with the laser beam from a double-jet dye laser (Coherent 702-CD) tunable in 285-310 nm region (SHG of Rhodamine 6G dye), synchronously pumped by a mode-locked, cavity dumped Nd:YAG laser (Coherent Antares 76). Fluorescence was then directed to a substractive double 0.25 m CVI monochromator and detected with the use of time-correlated single photon counting (TCSPC) equipped with an XP 2020 Phillips photomultiplier (effective temporal resolution of *ca.* 200 ps). The deconvolution of the decay parameters from the collected decay curves was achieved with the aid of home-written software (least-square fitting) allowing up to three-exponential analysis.

3. Analysis and discussion of the experimental results

All electronic absorption and fluorescence spectra in *n*-hexane, cyclohexane, and methanol solutions were always measured at room temperature. The used solvents differ greatly in their polarity, from non-polar (non-hydrogen-bonding) *n*-hexane and cyclohexane (dielectric constant $\varepsilon = 1.98$ and 2.02, respectively) to strongly polar and hydrogen-bonding methanol ($\varepsilon = 31.2$).

3.1. Absorption spectra

In Fig. 1 the absorption spectra of PHN and BQ in *n*-hexane are compared with an absorption spectrum of PH molecule in this solvent. The absorption spectrum of PH is composed of several strongly overlapping high-intensity bands, in the range of 33000–50000 cm^{-1}, with the band of the highest intensity centered at *ca.* 39800 cm^{-1} (with the extinction coefficient $\varepsilon = 60000$ M^{-1} cm^{-1}). In the low-energy part of the absorption spectrum (32200–28500 cm^{-1}), a very low-intensity band with a rich vibrational structure (of frequency of ≈ 700 cm^{-1}) is observed (cf. the inset in Fig. 1). The origin (0–0) transition of the absorption spectrum of phenanthrene is located at 28918 cm^{-1}; its absorption coefficient found in the present study is $\varepsilon = 215$ M^{-1} cm^{-1}, both these values — the position

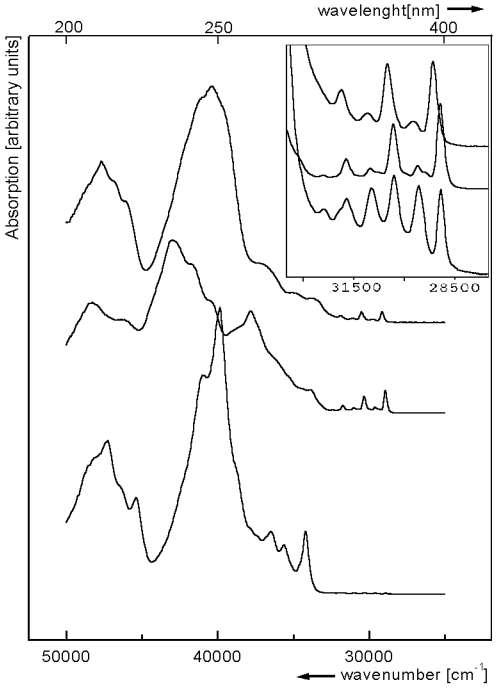


Fig. 1. Absorption spectra of phenanthrene, 7,8-benzoquinoline, and phenanthridine (from bottom to top, respectively) in *n*-hexane solutions. Intensities of absorption are not in scale (for the details concerning molecular extinction coefficient see Table I and the text). The inset is the blow-up of the first absorption band in the low-energy region of the absorption spectrum (32000–28500 cm^{-1}).

of (0,0) band and the molecular extinction coefficient are in very good agreement with the known values listed in spectral catalogues (see for instance [13]).

It can easily be noticed (cf. Fig. 1) that the absorption spectra of PHN and BQ in *n*-hexane solution bear very clear resemblance to the spectrum of PH in the whole UV spectral region from 28500–50000 cm^{-1} (350–200 nm), although they are as a whole blue-shifted (a hypsochromic shift). The position of the most intense band (with a maximum at ca. 39800 cm^{-1} in a phenanthrene spectrum) is visibly dependent on the position of the substitution of N atom in the ring system of phenanthrene. Its maximum is located at 40400 cm^{-1} (ε = 48000 M^{-1} cm^{-1}) and at 43000 cm^{-1} (ε = 38000 M^{-1} cm^{-1}) in the spectra of PHN and BQ molecules, respectively.

The fine vibrational structure of the first absorption band (32200–28500 cm^{-1}) is decreased in the spectra of PHN and BQ, as compared to the spectrum of phenanthrene (cf. the inset in Fig. 1), but some details are clearly seen. The blue shift (relative to the PH spectrum) of the origin (0–0) transitions in the case of BQ is very small, of *ca.* 17 cm^{-1}, but it amounts to *ca.* 220 cm^{-1} in the case of

PHN (cf. Table I) and this is just the opposite of the amount of shift of the maximum of the most intense band in the spectra. There is also a huge change of the extinction coefficient of the (0,0) band, from 215 M^{-1} cm^{-1} in the case of PH, to 5000 M^{-1} cm^{-1} and 2300 M^{-1} cm^{-1} in the case of BQ and PHN, respectively (cf. Table I). It is very clear that both, the blue shift of (0–0) transition and the change of its intensity in absorption spectra of azaphenathrenes under consideration, are dependent on the position of the substitution of N atom in the ring system of phenanthrene.

In Fig. 2 absorption spectra of BQ and PHN in all three solvents employed in this investigations, are given (for the sake of simplicity of further discussion only the low-energy part, i.e. only the first electronic absorption bands were reproduced). Numerical data relevant to this spectra were collected in Table I. The inspection of Fig. 2 and data of Table I shows that low-polarity solvents shift of the (0-0) transition is very small — a red shift of 33 and 17 cm^{-1} for BQ and PHN, respectively upon going from *n*-hexane to slightly more polar cyclohexane. However, in methanol solution the red shift of (0,0) absorption band of both molecules is noticeably different. For BQ molecule the total red shift of (0,0)

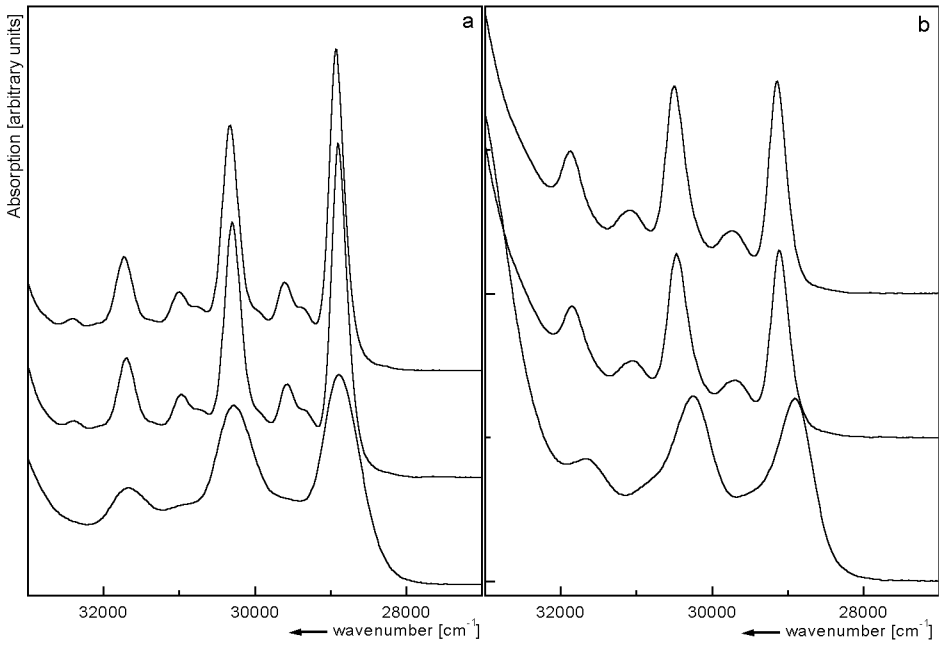


Fig. 2. The first absorption band ($S_0 \rightarrow S_1$ electronic transition) of 7,8-benzoquinoline (a) and phenanthridine (b) in *n*-hexane, cyclohexane and methanol solutions (from top to bottom, respectively). Intensities of absorption are not in scale (details about extinction coefficients are to be found in Table I and in the text).

TABLE I

Wavenumbers of the (0,0) bands in absorption ($\tilde{\nu}_A$) and fluorescence ($\tilde{\nu}_F$) spectra of phenanthrene (PH), 7,8-benzoquinoline (BQ), and phenanthridine (PHN) in different solvents. The molecular extinction coefficient (ε [M^{-1} cm^{-1}]) corresponding to each (0,0) band in the absorption spectrum is also given.

Solvent	PH			BQ			PHN		
	$\tilde{\nu}_A$ (cm^{-1})	ε	$\tilde{\nu}_F$ (cm^{-1})	$\tilde{\nu}_A$ (cm^{-1})	ε	$\tilde{\nu}_F$ (cm^{-1})	$\tilde{\nu}_A$ (cm^{-1})	ε	$\tilde{\nu}_F$ (cm^{-1})
n-hexane	28918	215	28884	28935	5000	28845	29137	2292	29091
cyclohexane	–	–	–	28902	5206	28845	29120	2015	29054
methanol	28902	321	28845	28885	2657	28440	28902	1969	28649

absorption band between *n*-hexane and methanol amounts to 50 cm^{-1}, but for PHN molecule it reaches the value of 235 cm^{-1}. We notice that the changes of the intensity of absorption (cf. extinction coefficients in Table I) of the (0–0) transition are more pronounced for BQ than for PHN molecule (drop of intensity, upon going from *n*-hexane to methanol solution, by *ca.* 47% and 15% for BQ and PHN, respectively).

Visually, a very noticeable change in the absorption spectra of both molecules in methanol is the loss of the vibrational structure and broadening of vibrational bands, due to their effective overlapping — a half-width of relatively sharp and intense (0,0) band, which in *n*-hexane is 240 and 280 cm^{-1} in the spectrum of BQ and PHN, respectively, becomes in methanol as large as 640 cm^{-1} in the case of BQ spectrum. In the case of PHN, the (0,0) band acquires in methanol an asymmetric envelop (with a second vibrational component hidden underneath) and its half-width, exceeding 1000 cm^{-1} , cannot be reliably determined at all.

This review of present investigations of the behavior and the main features of the absorption spectra of BQ and PHN observed in different solvents can be briefly summarized as follows: the influence of different solvents on the absorption spectra of studied azaphenanthrenes is rather moderate (especially in view of well-known tremendous effects for such monoazaanthracene molecule as acridine, observed upon going from aprotic to protic solvents [4]). Nevertheless, the changes observed in methanol solutions are quite clear. We notice that the observed solvent shift of the (0,0) absorption band as well as the blurring of vibrational structure of the first absorption band ($S_0 \rightarrow S_1$ transition) is more pronounced in the case of PHN molecule. In terms of intermolecular interactions between lone-pair electrons of nitrogen atom and solvent molecules, PHN molecule can presumably be treated as more active or more approachable (having less steric hindrance) than BQ molecule, which can also be inferred from the comparison of their structures. However, the observed absorption spectra do not provide any direct evidence of specific interactions (such as hydrogen bond formation) between solvent molecules and lone-pair n electrons of the solute molecules. The excitation from the ground, S_0, to the

first excited singlet state, S_1, seems to bear all characteristics of $\pi \rightarrow \pi^*$ electronic transition, and it is probable that the observed spectral changes could be accounted for with the aid of universal solvent–solute interactions.

3.2. Fluorescence spectra

We must start with the remark that the shape of fluorescence band of investigated molecules is strongly dependent on their concentration in the solution (this effect will be discussed elsewhere) and that all fluorescence spectra reproduced in this paper were registered for diluted solutions (with a concentration of 5×10^{-5} M).

In Fig. 3 the fluorescence spectra of BQ and PHN observed in *n*-hexane, cyclohexane, and methanol solutions are given. It can easily be noticed that for both molecules the fluorescence spectrum is shifting as a whole towards lower energies (a red-shift), following the increase of the polarity of solvents (cf. also positions of fluorescence (0,0) band listed in Table I). We notice that going from *n*-hexane to methanol solution produces almost the same amount of the red shift of (0,0) fluorescence band for both molecules, i.e. 405 and 442 cm^{-1} in the case

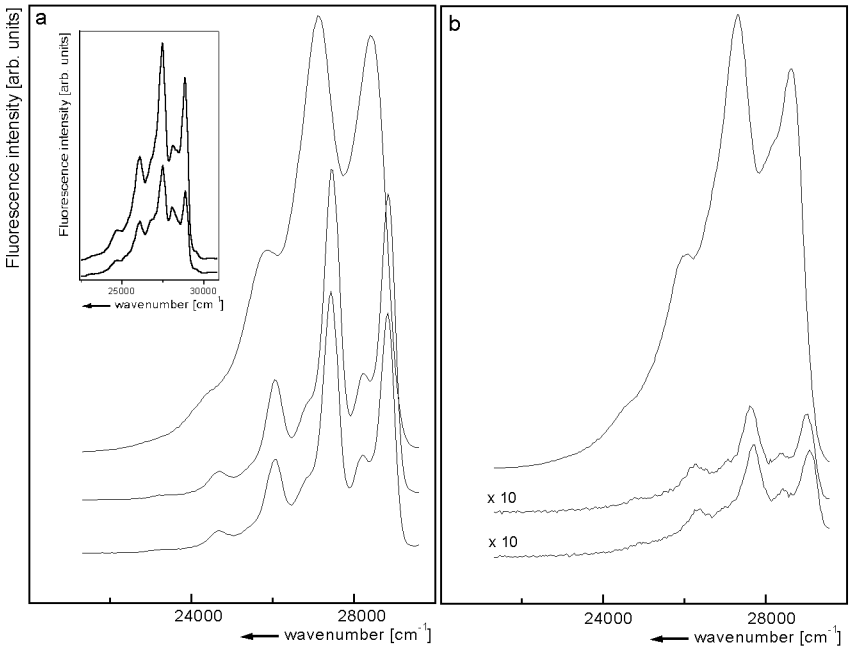


Fig. 3. Fluorescence spectra of 7,8-benzoquinoline (a) and phenanthridine (b) in *n*-hexane, cyclohexane, and methanol solutions (from bottom to top, respectively). Fluorescence intensities of the spectra are in scale. For comparison in the inset the fluorescence spectra of phenanthrene in *n*-hexane (bottom) and in methanol (top) solutions are shown.

of BQ and PHN, respectively. And similarly to the case of the absorption spectra, a fairly sharp vibrational structure of fluorescence bands observed in non-polar and aprotic solvents (*n*-hexane, cyclohexane), is getting less pronounced in more polar, protic methanol (for comparison, the inset in Fig. 3a shows the fluorescence spectra of phenanthrene in both solvents, with no visible solvent effect on the vibrational structure).

There is, however, a great difference between these two molecules in the observed intensity change caused by switching from *n*-hexane to methanol solution, as illustrated in Fig. 3, for both molecules an integrated intensity of the fluorescence band is increasing, between *n*-hexane and methanol solution, approximately by the factor of 4 in the case of BQ and by the factor of 40 in the case of PHN. And this once again points out that the position of the substitution of N atom in azaphenanthrenes can play a decisive role in the observed changes of their spectral parameters.

3.3. Analysis of the Stokes' shift

As discussed earlier in preceding Sects. 3.1 and 3.2, the (0,0) origin bands of absorption and fluorescence spectra of both molecules are shifting toward lower energies (red shift), following the increase in solvent's polarity (cf. Table I). Since the red shifts of the (0,0) bands of absorption and of fluorescence spectra are different in different solvents, and different for both molecules, the resulting net shift, or Stokes' shift ($\Delta\tilde{\nu}_S = \tilde{\nu}_A - \tilde{\nu}_F$) between the absorption ($\tilde{\nu}_A$) and fluorescence ($\tilde{\nu}_S$) (0,0) bands, is also different. This is illustrated in Fig. 4, where the absorption and fluorescence spectra of both molecules in *n*-hexane and methanol solutions are compared. It is seen that there is an approximate mirror-image relationship between absorption and fluorescence spectra of both azaphenanthrenes. In non-polar *n*-hexane solution the Stokes' shift is small and the (0,0) bands of absorption and fluorescence are nearly coinciding. In polar methanol solution the Stokes' shift is much larger than in *n*-hexane and amounts to 445 cm^{-1} for BQ molecule and to 253 cm^{-1} for PHN molecule (cf. also Table II).

With no clear evidence that could indicate the presence of specific solvent–solute intermolecular interactions (such as the formation of the hydrogen bond or intermolecular complexes) in the studied cases, the observed spectral changes and differences between BQ and PHN molecules can probably be accounted for in terms of universal interactions within the framework of the Onsager theory of dielectrics [14]. There are many versions and theoretical or semi-empirical modifications of the relationship between the Stokes' shift and the static dielectric constant, ε, and refractive index, n, of the solvent which could be applied in order to describe the present observations (see for instance [15–17]). However, the case of BQ molecule was studied and analyzed, in a large series of solvents, as early as 30 years ago [18], and for the obvious reason of reference we will stick to the modification developed by Bilot and Kawski [19]. Hence, with the assumption that

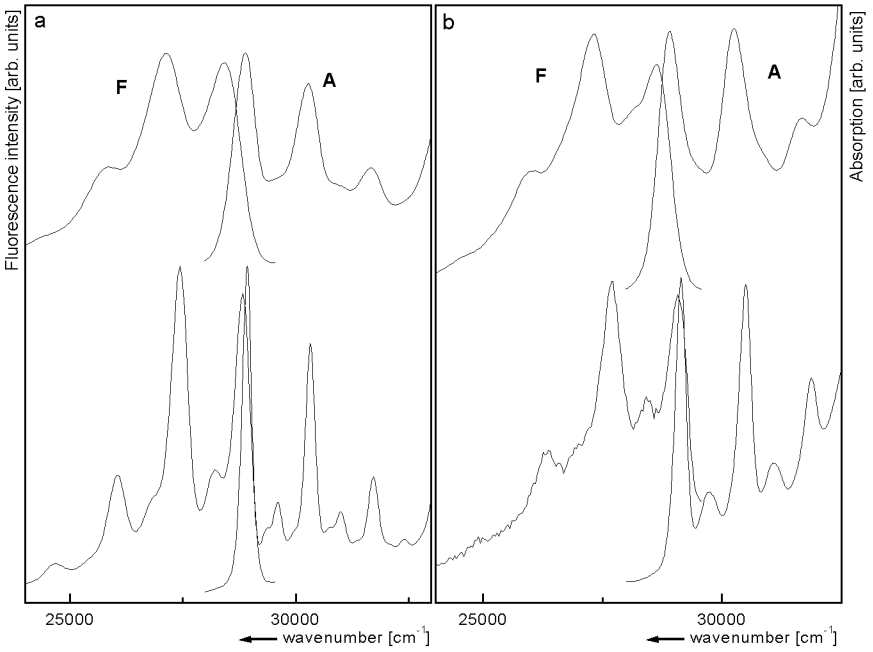


Fig. 4. Illustration of approximate mirror-image relationship between absorption (A) and fluorescence (F) spectra of 7,8-benzoquinoline (a) and phenanthridine (b) in n-hexane and methanol solutions (from bottom to top, respectively).

there are no specific solvent–solute interactions, for the description of the Stokes' shift in different solvents we use an expression of the following type:

$$\Delta\tilde{\nu}_{\mathrm{S}} = \tilde{\nu}_{\mathrm{A}} - \tilde{\nu}_{\mathrm{F}} = m_1 \cdot f(\varepsilon, n) + \text{const.}, \tag{1}$$

where $\tilde{\nu}_{\mathrm{A}}$ and $\tilde{\nu}_{\mathrm{F}}$ are the wave numbers of the (0,0) bands of absorption and fluorescence, respectively. The solvent dielectric function, $f(\varepsilon, n)$, is given as

$$f(\varepsilon, n) = \frac{2n^2+1}{n^2+1}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right), \tag{2}$$

where ε is the static dielectric constant and n is the refractive index of the solvent. The m_1 term in Eq. (1) is given as

$$m_1 = \frac{2(\boldsymbol{\mu}_{\mathrm{e}} - \boldsymbol{\mu}_{\mathrm{g}})^2}{hca^3} \tag{3}$$

and describes the change of the vector of electric dipole moment between the ground ($\boldsymbol{\mu}_{\mathrm{g}}$) and excited ($\boldsymbol{\mu}_{\mathrm{e}}$) state, caused by the excitation of molecule, which occupies a spherical cavity, of a radius a, in a given solvent (taken in the calculations as being equal to 4 nm). As always, the constants h and c are the Planck constant and the velocity of light in vacuum, respectively.

The plots of the observed Stokes' shifts, $\Delta\tilde{\nu}_{\mathrm{S}} = \tilde{\nu}_{\mathrm{A}} - \tilde{\nu}_{\mathrm{F}}$, versus $f(\varepsilon, n)$ function of the solvents, for both molecules under consideration, are shown in Fig. 5. The m_1 term, extracted for BQ molecule from the plot in Fig. 5, is $m_1 = 446\ \mathrm{cm}^{-1}$, and this result is in excellent agreement with the result ($m_1 = 450\ \mathrm{cm}^{-1}$) found earlier in Ref. [18]. And, as in the cited work, the value of the change of electric dipole moment between the ground and excited state, $|\Delta\boldsymbol{\mu}| = |\boldsymbol{\mu}_{\mathrm{e}} - \boldsymbol{\mu}_{\mathrm{g}}|$, would equal to 1.69 D, provided that both vectors remain parallel in both states under consideration. The analysis of the solvent shifts, carried out separately for the absorption and fluorescence spectra [18], has delivered the following values for electric dipole moments in the ground and first excited singlet states: $\mu_{\mathrm{g}} = 0.52$ D and $\mu_{\mathrm{e}} = 2.19$, i.e. the values very consistent with the value of the change of dipole moment obtained from the analysis of the Stokes' shift. On the other hand, recent calculations performed for BQ molecule have delivered 1.85 D as the value of the ground-state electric dipole moment [20], which greatly differs from the above findings (and such discrepancy may be considered as an indication that the present theoretical methods are still not accurate enough to cope with the problem).

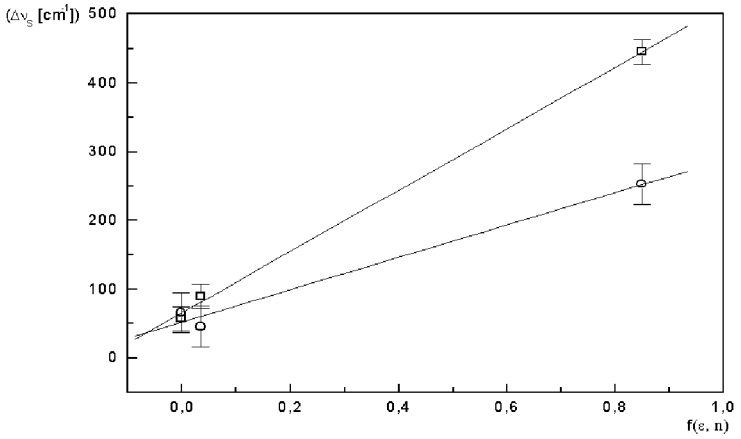


Fig. 5. Stokes' shift between the origin (0,0) bands of absorption and fluorescence of 7,8-benzoquinoline ((□) and phenanthridine (○) in different solvents (Eq. (1))).

As it is seen in Fig. 5 the plot of the Stokes' shift for PHN molecule is different from that of BQ molecule. In this case a value of m_1 term, Eq. (3), is $m_1 = 235\ \mathrm{cm}^{-1}$ and this lead to the value of the change of electric dipole moment between the ground and excited state, $|\Delta\boldsymbol{\mu}| = |\boldsymbol{\mu}_{\mathrm{e}} - \boldsymbol{\mu}_{\mathrm{g}}| = 1.25$ D. At this stage of investigations, and in view of the lack of any reference data (neither experimental nor theoretical) about the dipole moments of PHN molecule, we would like to refrain from any guesses about the electric dipole moments of PHN molecule in its ground and first excited singlet states, especially those based on the assumptions about the same parallel orientation of these vectors in both states combining in

the electronic (absorption and fluorescence) transitions. First, one has to learn how the different positions of N atom substitution into the aromatic structure of phenanthrene determine the equilibrium structures and charge distributions in both monoazaphenanthrenes.

3.4. Decay times of fluorescence and photophysical parameters of excited state

Measurements of the decay time of fluorescence of BQ and PHN molecules have been carried out in a way described in Sec. 2, for their solutions in *n*-hexane and in methanol. A typical observed decay curve (time profile) of fluorescence is illustrated in Fig. 6, and the decay times retrieved from the decay curves are collected in Table II.

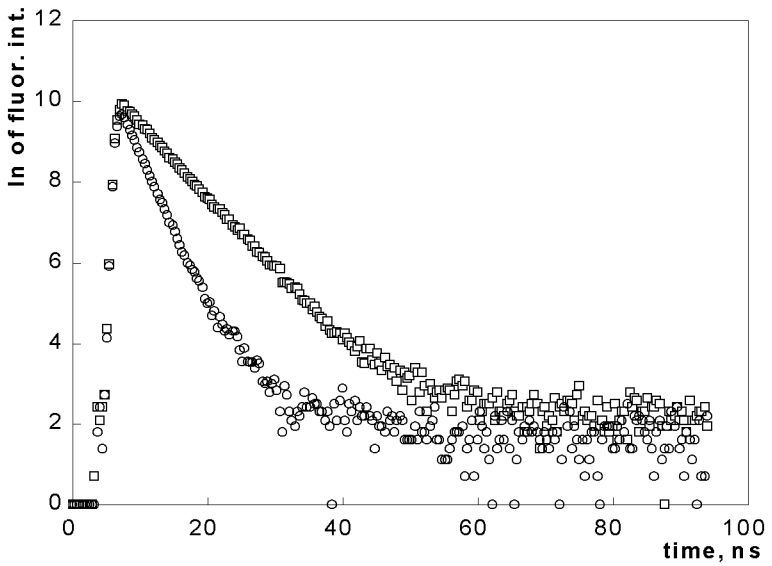


Fig. 6. Decay curves of fluorescence of 7,8-benzoquinoline in *n*-hexane (○) and methanol (□) liquid solutions.

In *n*-hexane solution the decay times of fluorescence of PHN were very short, shorter than 500 ps, which is the practical time resolution limit of our experimental setup for reliable determination of the decays of weak emission. The decay times of fluorescence of both molecules are getting longer in methanol solution. The analysis of the decay curves reveals only a single-exponential behavior (with a typical χ^2 value less than 3.0). And practically (i.e. within the error limit) the decay times of fluorescence are independent of the wavelength of observation (monitoring) of fluorescence, within the entire fluorescence band.

A change of the observed decay time of fluorescence, $\tau_{\rm d} = 1/(k_{\rm f} + k_{\rm nr})$, upon going from *n*-hexane to methanol solution can be due to the changes of the rates

of either the radiative, k_{f}, or nonradiative, k_{nr}, processes, or both of them. In order to distinguish between these two deactivation channels of the excited state of molecule, in addition to the decay time of fluorescence one has to know the quantum yield of fluorescence. In the present investigations we have not been able (for experimental reasons) to determine the quantum yields of fluorescence, and instead we have used another method of determination of the k_{f} rate constant (or mean radiative lifetime of fluorescence, $\tau_{\mathrm{f}} = 1/k_{\mathrm{f}}$). A general consideration of the kinetics of the process of fluorescence emission relates the radiative lifetime τ_{f} to the extinction coefficient of the corresponding absorption band. As always in the case of semi-empirical treatment of the data, a variety of different formulae were derived (of more or less general character) that can be used for extracting the radiative lifetime of fluorescence from the observed absorption band (see for instance [12, 21–23]). In the present work we observe an approximate mirror-image relationship between the fluorescence bands and the first absorption bands (cf. Fig. 4). Furthermore, the first absorption band ($S_0 \rightarrow S_1$ electronic transition), although of low intensity, is not hidden under the much more intense absorption bands (electronic transitions to higher excited states). Under these circumstances, for estimations of the radiative lifetimes, we can safely use a very handy formula which was derived by Förster [21]

$$k_{\mathrm{f}} = 2900n^2 \int \frac{(2\tilde{\nu}' - \tilde{\nu})^3}{\tilde{\nu}} \varepsilon \mathrm{d}\tilde{\nu}. \tag{4}$$

In this formula, $\tilde{\nu}'$ is the wave number of the mirror symmetry point (crossing-point) between the absorption and fluorescence bands (cf. Fig. 4), n is the refractive index of the solvent and ε is the molecular extinction coefficient. The integration runs over the whole absorption band (corrected for the asymmetry). The rate constants of radiative transition, calculated in this way, for both molecules in n-hexane and methanol solutions are given in Table II, together with the subsequently calculated rate constant, k_{nr}, for nonradiative transition.

The inspection of data of Table II reveals the fact that the radiative rate constants of BQ and PHN molecules are comparable in non-polar n-hexane so-

TABLE II

Stokes' shifts ($\Delta\tilde{\nu}_{\mathrm{s}}$) between the absorption and fluorescence spectra, decay times of fluorescence (τ_{d}), and radiative (k_{f}) and nonradiative (k_{nr}) rate constants for 7,8-benzoquinoline (BQ) and phenanthridine (PHN) in n-hexane and methanol solutions.

Solvent	BQ				PHN			
	$\Delta\tilde{\nu}_{\mathrm{S}}$ (cm^{-1})	τ_{d} (ns)	k_{f} (s^{-1})	k_{nr} (s^{-1})	$\Delta\tilde{\nu}_{\mathrm{S}}$ (cm^{-1})	τ_{d} (ns)	k_{f} (s^{-1})	k_{nr} (s^{-1})
n-hexane	90	2.6	2.9×10^7	3.5×10^8	46	< 0.5	2.2×10^7	$> 2 \times 10^9$
methanol	445	5.3	2.8×10^7	1.6×10^8	253	3.9	2.6×10^7	2.3×10^8

lution, as well as in a strongly polar methanol solution. For both molecules the decay time of fluorescence increases in methanol solution, although this increase being moderate (by the factor of 2) in the case of BQ molecule, seems to be much larger in the case of PHN molecule (changing from the presumably subnanosecond range in *n*-hexane, to the nano-second range in methanol). Hence, the change of the rate constant for nonradiative decay in methanol solution is larger for PHN molecule than that for BQ molecule. This piece of information, which is at the moment only of a qualitative character (as we mentioned earlier the decay times of PHN molecule in *n*-hexane solution were below the limit of time resolution of our present apparatus), is consistent with the observed huge enhancement of the fluorescence intensity of PHN in methanol solution in comparison with *n*-hexane solution (cf. discussion in Sec. 3.2). An unavoidable conclusion of such observation is that in methanol solution non-radiative decay channels of the first excited singlet state are becoming less effective, especially in the case of PHN molecule. Such an effect could presumably be related to a different change of the electronic (as well as geometrical) structure and/or to different ordering of the electronic states within the excited states manifold (singlets and triplets of $\pi\pi^*$ and $n\pi^*$ character) induced in both molecules by the methanol–solute interactions.

4. Final remarks

The results of our investigations of the behavior of absorption and fluorescence spectra of phenanthridine and 7,8-benzoquinoline in non-polar (and non-hydrogen bonding) *n*-hexane solution and in strongly polar (and hydrogen-bonding) methanol solution are rather clearly showing that the first excited singlet state in both molecules is of $\pi\pi^*$ character. The influence of solvent on spectral characteristics of both molecules is moderate and no evidence of specific solvent–solute interactions (of the type of hydrogen-bond formation or excited-state protonation reaction) could be inferred from the observed spectra. The observed solvents shifts of the absorption and fluorescence bands and the Stokes' shift between these bands can be accounted for in terms of universal (dielectric) solvent–solute interactions.

However, the observed differences in solvent influence on the fluorescence spectra of both molecules, such as different amounts of the solvent shifts and differences in the change of the electric dipole moments between their ground and excited states, seem to indicate the key role of the position of the substitution of N atom into aromatic system of phenanthrene (parent hydrocarbon for both studied monoazaphenanthrenes). This conclusion seems to be also confirmed by the estimated different changes of the nonradiative processes in the first excited state of both molecules in methanol solution.

But for a deeper insight and understanding of such effects, one needs a more detailed knowledge of how the electronic, as well as the geometrical structures and other molecular parameters of studied azaphenanthrenes are dependent (if at all)

on the position of the substitution of nitrogen atom and this is now in the course of investigations.

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References

[1] E.J. Bowen, J. Saha, *J. Chem. Soc.* , 3716 (1958).

[2] S.P. McGlynn, *J. Chem. Phys.* **37,** 1825 (1962).

[3] S.J. Ladner, R. Becker, *J. Phys. Chem.* **63,** 2481 (1963).

[4] L.A. Diverdi, M.R. Topp, *J. Phys. Chem.* **83,** 3447 (1984).

[5] J. Prochorow, I. Deperasińska, O. Morawski, *Chem. Phys. Lett.* **316,** 24 (2000).

[6] J. Prochorow, I. Deperasińska, O. Morawski, *J. Mol. Struct.* **555,** 97 (2000).

[7] I. Deperasińska, J. Prochorow, *Acta Phys. Pol. A* **100,** 845 (2001).

[8] M. Nakamizo, *Spectrochim. Acta* **22,** 2039 (1966).

[9] A. Grabowska, B. Pakuła, J. Panciř, *Photochem. Photobiol.* **10,** 615 (1969).

[10] E. Vander Donckt, R. Dramaix, J. Nasielski, C. Vogels, *Trans. Faraday Soc.* **65,** 3258 (1969).

[11] C.J. Marzacco, G. Deckey, R. Colarulli, G. Siuzdak, A.M. Halpern, *J. Phys. Chem.* **93,** 2935 (1989).

[12] R.S. Becker, *Theory and Interpretation of Fluorescence and Phosphorescence*, Wiley Interscience, New York 1969, ch. 5 and 6.

[13] *DMS UV Atlas of Organic Compounds*, Vol. 3, Verlag Chemie GmBH, Butterworth, London 1967, pos. E3/1,71 and H9/1.

[14] L. Onsager, *J. Am. Chem. Soc.* **58,** 1486 (1936).

[15] N.S. Bayliss, E.G. McRea, *J. Phys. Chem.* **58,** 1002 (1954).

[16] N. Mataga, Y. Kaitu, M. Koizumi, *Bull. Chem. Soc. Jpn.* **29,** 465 (1956).

[17] E. Lippert, *Z. Elektrochem.* **61,** 962 (1957).

[18] I. Janic, A. Kawski, *Bull. Acad. Pol. Sci., Ser. Sci. Math. Astr. Phys.* **XX,** 519 (1972).

[19] L.J. Bilot, A. Kawski, *Z. Naturforsch.* **17**a, 621 (1962).

[20] A.L. Mattioda, D.M. Hudgins, C.W. Bauschlicher, Jr., M. Rosi, L.J. Allamandola, *J. Phys. Chem. A* **107,** 1486 (2003).

[21] Th. Förster, *Fluoreszenz Organischer Verbindungen*, Vandenhoeck & Ruprecht, Göttingen 1951, p. 156.

[22] C.A. Parker, *Photoluminescence of Solutions*, Elsevier Publishing Co., Amsterdam 1968, ch. 1.

[23] J.B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Intersicence, London 1970, ch. 4.