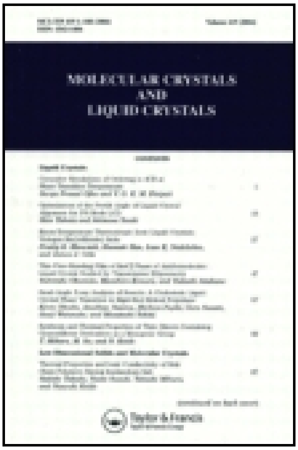

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Photothermal Properties of 3-Substituted Benzanthrone Dyes

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Photothermal Properties of 3-Substituted Benzanthrone Dyes

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The paper presents spectral properties of six 3-substituted benzanthrone dyes dissolved in ethanol. Absorption, fluorescence, photoacoustics and time-resolved photothermal spectroscopy were used to follow radiative and non-radiative deactivation pathways occurring in dyes with participation of their excited singlet and triplet states. Thermal deactivation parameters were evaluated. They show that global non-radiative deactivation of excited energy depends on a kind of peripheral groups attached to the main molecular core. The yields of triplet state population and times of thermal deactivation decay were estimated and discussed in terms of the conformational changes in dyes and the differences in the dye molecular structures.

Keywords: benzathrone dyes; photoacoustics; thermal deactivation; triplet state population

This paper is not published elsewhere and that it has not been submitted simultaneously for publication elsewhere.

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Abbreviation: B – benzanthrone, BCP – bromocresol purple, F – fluorescence, IC – intersystem crossing, ISC – internal conversion, LIOAS – laser induced optoacoustic spectroscopy, PAS – photoacoustic spectroscopy

1. INTRODUCTION

Benzanthrone dyes and their chemical analogues attract still a lot of attention due to their unique photophysical and photochemical behavior and also because of their potential wide applications [1,2]. These dyes are characterized by deep colour and high photostability and thus they are utilized in coloration of polymers [3], as disperse dyes for textiles [4] and fluorescence dyes [1].

Since these dyes can be quite easily chemically modified by different peripheral groups attached to the main molecular core we can control their photophysical properties. Recently, the basic spectral (absorption and fluorescence) properties of a family of 3-benzathrone derivative dyes were investigated [5,6] and it was shown that their spectroscopic and photochemical properties are very sensitive to a small variation in their molecular structure [6,7]. The absorption and fluorescence properties were mostly followed in several organic solvents, and also in polymeric film and nematic liquid crystals [5,6]. It was certainly indicated that in the non-polar solvents 3-benzathrone dyes are non-fluorescent species while in alcohols their weak fluorescence was observed. The absorbance feature is strongly influenced by the presence of the substituents linked to the benzathrone scaffold. Also the fluorescence quantum yields were also shown to be dependent on the dye molecular structure, i.e. on a kind of peripheral groups attached to the molecular frame [6,8].

As far as we know the photothermal properties of benzanthrone dyes were never investigated. Thus in this paper our attention will be focused on the thermal deactivations of the dye excited states as a result of non-radiative processes. This purpose we realized using both steady-state photoacoustic spectroscopy (to get information on the global photothermal processes occurring in dyes after light absorption [9]) and time-resolved photothermal method (named light–induced photoacoustic spectroscopy – LIOAS) which gives insight into the kinetics of the thermal deactivation pathways.

2. MATERIALS AND METHODS

The benzanthrone dyes were synthesized according to the procedure described in [10] and the molecular structure of dyes are shown in Figure 1.

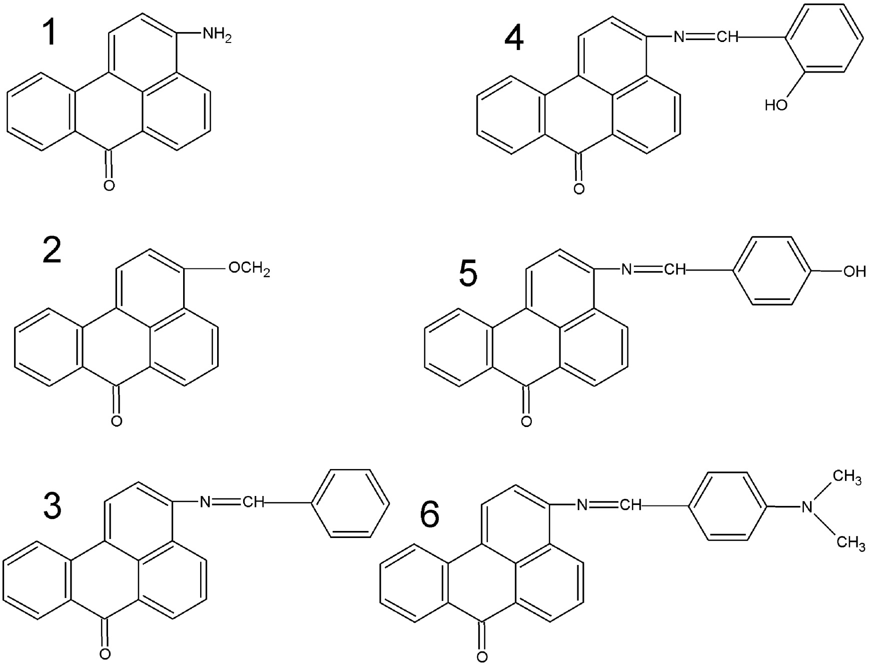

FIGURE 1 The molecular structures of 3–substituted benzanthrone dyes under study.

The absorption spectra were measured with the Specord M40 spectrophotometer (Carl Zeiss, Jena, Germany) in the range of 300–700 nm. Fluorescence was registered with the spectrofluorimeter Hitachi F4500 (Japan) in the region of 435–900 nm. The steady-state photoacoustic spectra were obtained with a single-beam photoacoustic spectrometer PAC300 (MTEC, Iowa, USA) at three light modulation frequencies: 8, 15, 30 Hz at the same phase shift: $\Phi = 20$ deg. Photoacoustic experiments were done in the helium atmosphere at room temperature.

The kinetics of photothermal processes and triplet state populations were studied with the laser-induced optoacoustic spectroscopy (LIOAS). In the LIOAS experiment the resolution of the apparatus is about 0.4 μs. Thus it is possible to distinguish prompt thermal effects occurring in the time range shorter than 0.4 μs from those which occur in the time longer than 0.4 μs. The pulse subnanosecond nitrogen laser was used as a light source. The solution of bromocresol purple (BCP) in ethanol was used as a standard sample on the supposition that whole energy absorbed by this dye is changed into heat in the time shorter than the resolution time of the apparatus [11]. The experiments were done at room temperature and in the oxygen and nitrogen atmosphere. The analysis of the photothermal signal was done using two methods. On the basis of the method elaborated by Rudzki-Small *et al.* [12] the deconvolution of the sample and reference responses for the exponential components of thermal deactivation (TD) was conducted. In the method proposed by Marti *et al.* [13] two waveform signals (for the dye and for a standard sample) were compared. In Marti's method the maximal amplitude of the signal is given by:

$$\mathrm{H_{max}} = \mathrm{k}\alpha \mathrm{E_L}(1 - 10^{-A}), \tag{1}$$

where k is a factor which includes the apparatus optical geometry, the electronic impedance of the system and the thermoelastic properties of the solvent, α is a part of energy changed promptly into heat, A is absorbance of the sample and $\mathrm{E_L}$ is laser light energy. The yield of the triplet state population (Φ_T) can be calculated from the equation:

$$\Phi_\mathrm{T}\mathrm{E_T} = (1 - \alpha)\mathrm{E_L} - \Phi_\mathrm{F}\mathrm{E_F}, \tag{2}$$

where: Φ_F is fluorescence quantum yield, $\mathrm{E_F}$ and $\mathrm{E_T}$ are energies of fluorescence and of triplet state with respect to the ground state, respectively. The LIOAS experiments were performed at the room temperature in nitrogen and oxygen atmosphere.

The dyes were dissolved in ethanol. The dye concentrations were: 0.01 mM, 0.1 mM and 1 mM and the spectroscopic measurements were done in the 1 cm, 1 mm and 60 μm quartz cuvettes, respectively.

3. RESULTS AND DISCUSSION

3.1. Absorption and Fluorescence Studies

Figure 2 presents the electronic absorption spectra of six investigated dyes dissolved in ethanol. The results are as expected and are in good accordance with the literature data [5,10]. The character of the spectra is related to the electron donor-acceptor interaction between the substituents and carbonyl group. The absorption properties of some 3-benzanthronic dyes were widely discussed in the paper [6] thus inhere we describe only briefly some basic features which are essential in the photothermal investigation.

All investigated dyes exhibit two pronounce absorption bands. It is clearly seen that absorption depends very strongly on a kind of the peripheral groups attached to the main benzanthronic core. Each dye absorbs markedly in the near UV region, while absorption in the longwavelength range (between 400–600 nm) depends on the electron donating group substituted at the C-3 position. The dyes **1** and **6**

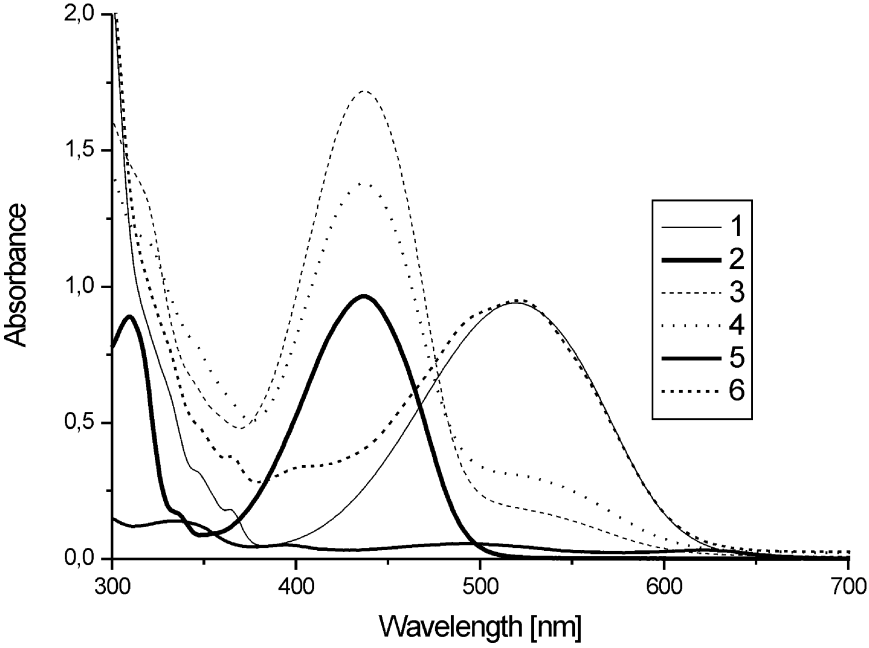

FIGURE 2 The absorption spectra of the investigated dyes in ethanol (c = 0.01 mM).

absorb strongly and show broad bands between 450 and 600 nm, whereas the remaining dyes exhibit the intensive absorbance in the range of 350–500 nm (an exception is the **5**). The long-wavelength band are described to the charge-transfer owing to the π-π^* intramolecular electron transfer in the S_0-S_1 transition.

The concentration dependence (in the range of 10 μM–1 mM) of absorption intensity indicates the domination of the monomeric dye species in solvent. The locations of the absorption band maxima are the same for dyes of different concentrations. The values of the half widths half-bandwidths estimated for the concentration range of 1 mM–10 μM confirm the supposition as to the domination of one molecular species in the samples since their values are almost independent of the dye concentration.

All investigated dyes show more or less intensive fluorescence (Fig. 3). The fluorescence intensities increase in accordance with the dye concentrations. Since the fluorescence is more sensitive than absorption for any changes occurring in the molecules we can claim that prompt radiative deactivation processes shown as fluorescence

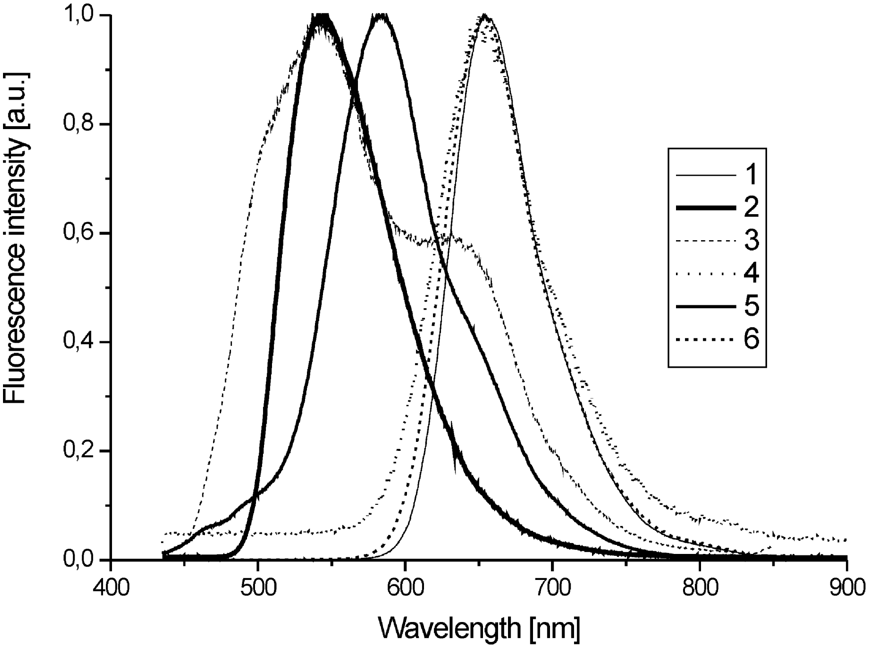

FIGURE 3 The normalized fluorescence spectra of the investigated dyes dissolved in ethanol. (c = 0.01 mM; all dyes were excited at $\lambda_{ex} = 410\,\text{nm}$)

originate from the monomeric dyes. The coincidence of the absorption and excitation spectra (not shown) gives additional confirmation on the existence of the monomers in solution.

Recently, Bhujle [14] showed the dependence of absorption and fluorescence changes with the dye concentration in alcoholic solvents and it was attributed to the creation of the aggregated dyes. However, we do not observe particular concentration changes since the straight lines of absorption and fluorescence signals in the range of 1 mM–10 μM is obtained.

These results seem to be important in the view of photothermal examination because thermal deactivation pathways are expected to be markedly different for monomeric and aggregated molecular moieties.

3.2. Photothermal Examinations

The example of photoacoustic spectra (PAS) of dyes at 8 Hz light modulation frequency is presented in Figure 4. The photoacoustic measurements were done at three light modulation frequencies (8, 15 and

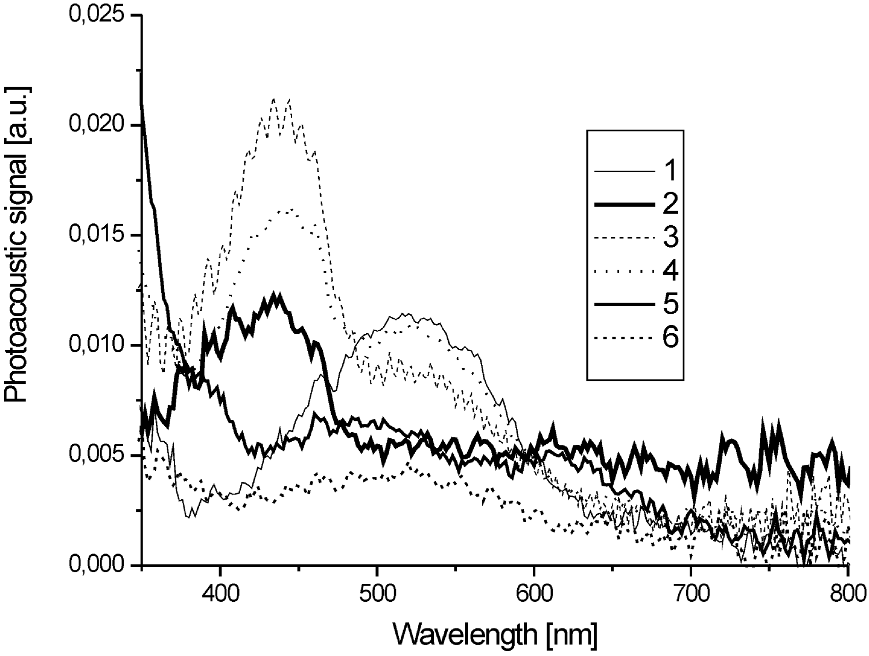

FIGURE 4 The photoacoustic spectra of the investigated dyes at 8 Hz light modulation frequency (c = 1 mM).

30 Hz) and for two dye concentrations (1 mM and 0.1 mM). The absorption and photoacoustic spectra show very good coherence. Thermal deactivation parameters (TD), presented in Table 1, are estimated as a ratio of photoacoustic signal to absorbance. The highest TD values observed for the dyes **5** and **6** indicates the strong influence of the peripheral groups on thermal deactivation. On the other hand the fluorescent dye **2** exhibits the low thermal deactivation owing to competition between radiative and non–radiative processes. The low TD value estimated for **4** could be connected with the existence of the intramolecular hydrogen bonding and it is discussed later in this paper. According to Rosencwaig–Gersho theory [9] the product of the photoacoustic signal and the square root of the light modulation frequency is expected to be constant provide that one dye species is responsible for thermal deactivation which occurs as a prompt non-radiative process. It is the case for our samples. The correlation factor between the experimental data and theoretical prediction reaches nearly unity (Table 1) what clearly indicates that only one spectral form of dye participates in thermal deactivation with high domination

TABLE 1 The Spectral Parameters of Non-radiative Deactivation Pathways of the Excited States of the Investigated Dyes

Dye	TD [a.u.]	r	α	Φ_T	k_1	τ_1[μs]	k_2	τ_2[μs]	α^*	Φ_T^*	k_1^*	τ_1^*[μs]	k_2^*	τ_2^*[μs]
1	1.22	0.99	0.76	0.23	0.79	≤ 0.4	0.07	2.3	0.48	0.24	0.47	≤ 0.4	0.02	≤ 0.4
2	0.86	0.98	0.61	0.11	0.64	≤ 0.4	0.01	8.2	0.75	0.09	0.67	≤ 0.4	0.09	≤ 0.4
3	1.23	0.99	0.57	0.18	0.57	≤ 0.4	0.11	≤ 0.4	0.57	0.20	0.75	≤ 0.4	0.22	≤ 0.4
4	0.56	0.99	0.62	0.25	0.66	≤ 0.4	0.20	13.1	0.71	0.22	0.78	≤ 0.4	0.01	≤ 0.4
5	3.20	0.99	0.59	0.15	0.56	≤ 0.4	0.07	≤ 0.4	0.74	0.21	0.78	≤ 0.4	0.06	≤ 0.4
6	4.20	0.98	0.43	0.25	0.48	≤ 0.4	0.01	1.1	0.62	0.22	0.68	≤ 0.4	0.01	≤ 0.4

$\Delta TD = \pm 0.05$, $\Delta r = \pm 0.01$, $\Delta\alpha = \pm 0.06$, $\Delta\Phi_T = \pm 0.10$, $\Delta k_1 = \pm 0.01$, $\Delta k_2 = \pm 0.01$, $\Delta\tau_2 = \pm 0.01$.

* – concerns the data in the oxygen atmosphere.

TD – thermal deactivation parameter.

r – correlation factor.

α/α^* – a part of the excited energy changed promptly into heat (obtained on the basis of Marti *et al.* method [13]).

Φ_T/Φ_T^* – the triplet state population quantum yield (obtained on the basis of Marti *et al.* method [13]).

k_1/k_2 – preexponential factors (obtained on the basis of Rudzki-Small *et al.* method [12]).

τ_1, τ_2 – decay times (obtained on the basis of Rudzki-Small *et al.* method [12]).

of the prompt processes in which the excited dye singlet states are involved.

The potential contribution of the metastable triplet states in non-radiative processes can be evaluated by the use of two procedures: proposed by Marti *et al.* [13] and Rudzki-Small *et al.* [12]. The experimental LIOAS waveforms in the nitrogen atmosphere is presented in Figure 5. In this experiment bromocresol purple (BCP) was used as a standard under supposition that whole energy absorbed by this dye is changed into heat in the prompt processes ($\alpha = 1$). All parameters which describe the thermal processes are gathered in Table 1. The α/α^* parameters (Marti *et al.* [13]) correspond to the k_1 values (Rudzki-Small *et al.* [12]) and they are similar in value in the accuracy of estimation. As seen the molecular substituents in the benzene ring have marked influence on the thermal properties of the benzanthronic dyes. The α/α^* parameters, describe a part of energy deactivated promptly (with the excited singlet state participation) and slowly (with the triplet state contribution). The α parameters vary from 0.76 to 0.43 depending on dyes. The highest α was evaluated for **1** and indicates that almost whole absorbed energy is changed into heat in the prompt processes. This result is consistent with the fluorescence behaviour of this dye; its fluorescence quantum yield is extremely low (in the

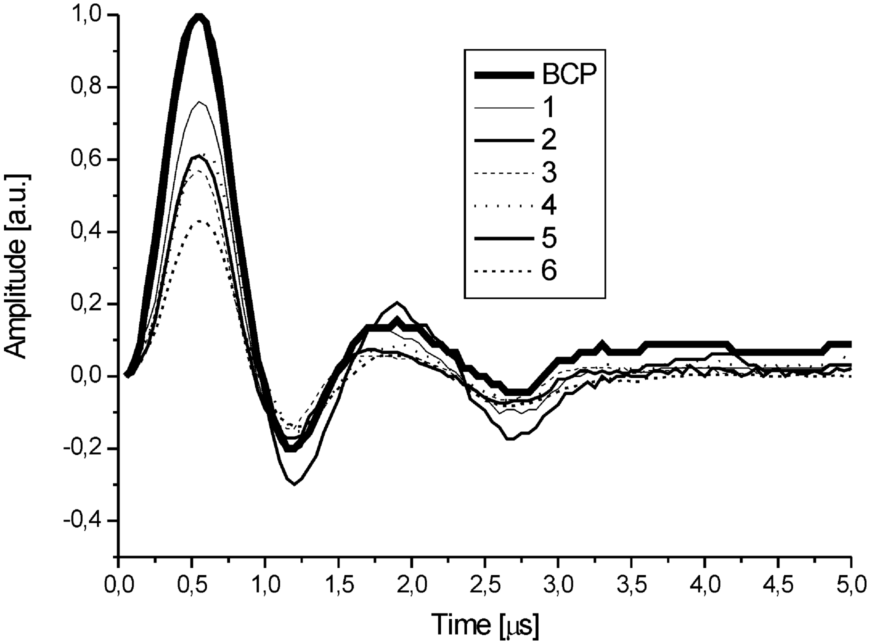

FIGURE 5 LIOAS waveforms of the dyes in ethanol under the nitrogen atmosphere. Bromocresol purple (BCP) was used as a standard.

accuracy of the experiment presented in [5]). The high value of the α parameter and low fluorescence quantum yield show clearly domination of non-radiative deactivation when the dye undergoes from the excited state to the ground state. The dye **3** with no substituents at the benzene ring and the dye **6** with electron donating dimethylamino group in p-position are characterized by the lowest α parameters (0.57 and 0.43, respectively) when compared with those for the remaining dyes.

Among investigated dyes, the dye **2** is characterized by the high fluorescence quantum yield ($\Phi_F = 0.55$ [5]). The high Φ_F was discussed in terms of the influence of the oxy group directly linked to the benzanthronic scaffold.

In accordance with Rudzki-Small *et al.* procedure we are able to estimate the yield of triplet state population [12]. The values do not excess 0.25 and depend slightly on a kind of dye. Even that the Φ_T values are not very high, it is clear that the triplet state is not very much involved in thermal processes of deactivation, however cannot be neglected.

The deconvolution procedure gives also information on kinetics of thermal deactivation. Two decay times were obtained: the first one, τ_1 is less than 0.4 µs (we are not able to distinguish the shorter time due to the LIOAS device resolution) and the second time, τ_2 is in the range of microseconds. These τ_2 values are in good accordance with the literature data for similar benzanthrone dyes [15]. The evaluated decay times are collected in Table 1. As seen, the values τ_2 are significantly affected by a kind of substituents. The fastest decays are characteristic for the dyes **3** and **5** and they are beyond the time resolution of the LIOAS experiment. However, this result could confirm the weak contribution of the triplet state in thermal deactivation in these dyes. It is not a case for the remaining dyes. The τ_2 of 8.2 µs (dye **2**) and 13.1 µs (dye **4**) are similar to those as found by the flash photolysis of 3–methoxybenzanthrone in methanol [15].

In our experiment, the sum of k_1 and k_2 does not reach unity. This result can suggest that in addition to unimolecular triplet decay other processes in which triplet states can occur: (i) generation of singlet oxygen, (ii) other processes occurring in the time range above 0.4 µs and/or triplet-triplet annihilation, (iii) conformation changes in the dye molecular structure, (iv) solvent volume changes. Point (i) could be quite easily solved by the LIOAS experiment in the oxygen atmosphere. The results are collected in Table 1 (the data with asterisks) and they evidently show significant influence of oxygen on the dye triplet state features. The most important is the drastic diminishing in the decay time τ_2 upon oxygen condition. These values drop markedly down beyond the time resolution of our LIOAS apparatus (0–4 µs). This could be explained as follows. The ground state in the oxygen molecule is the triplet state. And owing to the interaction with the dye triplet state, generation of the singlet oxygen cannot be neglected according to:

$$^3B^* + {}^3O_2 \rightarrow {}^1B + {}^1O_2, \qquad (3)$$

where B is a symbol of the benzanthrone molecule.

As a result the dye triplet state is quenched significantly by oxygen and it could explain short decay time in the oxygen presence. Although, the sum of k_1 and k_2 goes up of about 15–25% in the presence of oxygen but it does still not give 1. Thus points (ii)–(iv) are still under our consideration. As to point (ii) we should concern the phosphorescence and delayed luminescence processes. Phosphorescence at the room temperature and in not-viscouse solution can also be neglected, while delayed luminescence is rather not expected due to the large energy gap between S_1 and T_1 transitions as observed in other benzanthronic dyes [6]. The triplet-triplet annihilation is also unlike because in our experiments the flux of the light exciting beam is much lower than that required for the two-photon effects.

Point (iii) is consistent with the suggestion given in the papers [5,6,8,10] on the occurrence of the conformational changes in the molecular structure due to the strong donor-acceptor interaction and will be considered later in this paper. The changes of solvent volume (iv) affects all results in the same degree because each LIOAS experiment was done exactly under the same condition.

The question now arrives as to the low yield of generation of the dye triplet state for all investigated dyes. The quantum yield population depends strongly on the relation between the rates of intersystem crossing $S_1 \rightarrow T_1$ ($\mathrm{k_{ISC}}$), internal conversion ($\mathrm{k_{IC}}$) and fluorescence ($\mathrm{k_F}$) according to the equation:

$$\Phi_{\mathrm{T}} = \frac{\mathrm{k_{ISC}}}{\mathrm{k_{ISC}} + \mathrm{k_{IC}} + \mathrm{k_F}}. \tag{4}$$

For five dyes (**1**, **3–6**) fluorescence is not competitive with non-radiative decay because these dyes do practically not show fluorescence. Taking into account Eq. (2) and the estimated Φ_{T} values (of ca. 0.25–0.15) we have every reason to believe that internal conversion rate ($\mathrm{k_{IC}}$) is about 3–5 times larger than intersystem crossing rate ($\mathrm{k_{ICS}}$) for non-fluorescent benzanthronic dyes. On the other hand it is not doubt that fluorescence in the dye **2** should lead to the lower quantum yield Φ_{T} since decreasing $\mathrm{k_{ISC}}$ would tend to decrease Φ_{T}. It is confirmed by the lowest Φ_{T} values (0.11–0.09) for this dye. However, dissimilarity in the fluorescence behaviour indicates differentiation in the molecular conformational variations in **2** and in the remaining dyes. The photothermal and fluorescence behaviour confirms much less conformational changes in the dye **2** when compared with that of the remaining dyes.

It would be interesting to find the correlation between dye molecular structures and their triplet state features. In previous papers concerning photophysical properties of investigated dyes (absorption, fluorescence) it was evidently shown that spectroscopic behaviour of benzanthronic dyes are very sensitive to small changes in peripheral groups when dyes are substituted at position 3 [5–8]. As known the absorption and fluorescence properties markedly depend on a kind of the electron donating group at C-3 position. Thus we can suppose that modification of the photothermal and triplet state behaviour could also be affected by the peripheral groups attached to the main molecular benzanthronic core. Even that the Φ_{T} values are rather similar for all investigated dyes, the non-radiative decays are different (under nitrogen condition) and they vary from 0.4 μs to 13.1 μs.

Let come back to (iii). The dye **4** is characterized with the longest τ_2 time (13.1 μs) when compared with the remaining dyes. In this dye the electron donating OH-group at o-position and N atom at the C-3 position can form intramolecular hydrogen bonding [5]. It was suggested that this hydrogen bond is more stable in the S_1 excited state than that in the ground state S_0 [5]. In 3-substituted benzanthronic dyes triplet π-π^* transition is lower in energetic scale than the singlet π-π^* transition. Thus we can suggest that the hydrogen bonding could be more stable in T_1 excited state than in the ground state. This could explain the low TD value and quite long time decay of the triplet state when compared to other investigated dyes. Contrary, dyes **1**, **3**, **5** and **6,** in which such an intramolecular hydrogen bonding cannot occur, are characterized by very rapid deactivation transitions ($\tau_2 = 0.4 \div 2.3$ μs). The electron donor interaction in 3-benzanthronic molecules occurs between the electron acceptor carbonyl group and the electron donating group at C-3 position in the main molecular core. The electron donating OH and $N(CH_3)_2$ groups at p-position in the benzene ring (dyes **5** and **6**) enhance strongly electron donor-acceptor interaction [5,6]. Also in the dye **1** owing to the amino group the strong donor-acceptor interaction takes place. Such an effect is decreased by the presence of the azomethine group in the dye **3** [5,6]. In these dyes, the conformational changes are expected to be much like than that in the fluorescence dye **2**, and non-radiative deactivation could explain extremely rapid decay in which triplet states could be involved.

The dye **2** is the only dye, among others, which show radiative fluorescence and this thermal decay is quite long (8.2 μs). As mentioned above this oxy substituted benzathrone dye fluoresces owing to the less conformation transient. This could be a reason of the not so rapid deactivation decay by the triplet state.

4. CONCLUDING REMARKS

The photothermal properties of a number of 3-substituted benzanthronic dyes in ethanol were investigated. The electron donating substituents have not only influence on the absorbance and fluorescence features as shown in paper [5,10], but also the triplet state properties are strongly affected by them.

It was shown that internal conversion processes dominates over the deactivation *via* the triplet states in intersystem crossing transitions. The triplet state generation in the investigated dyes is rather low and its value does not excess 0.25. The triplet state thermal decays is also rather fast (13–0.4 μs) and indicate rapid deactivation of the dye excited states.

The photothermal properties are strongly influenced by the peripheral groups attached to the main benzanthrone core. Moreover it was indicated that a part of absorbed energy is used for conformational changes of dyes.

The absorption, fluorescence features studied before [5,6,10] and the photothermal results presented in this paper indicate that these benzanthronic dyes could be interesting as dyes in display systems but not in e.g., medicine as photosensitizers in cancerous therapy due to their low triplet state population and rapid decay time of the triplet state.

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