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Spectroscopic investigation of new benzanthrone luminescent dyes

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Luminescent dyes have received a considerable attention for their potential applications in biochemical and medical assays. Benzanthrone dyes are a special class of environmentally sensitive, photostable, bright luminophores. In the present research the photophysical properties of benzanthrone derivatives with amidine group and bromine atom in various positions were investigated and compared. The absorption and luminescence spectra in several organic solvents with various polarities were recorded and analyzed. Interesting results about substituent effects on the physical properties of the prepared dyes are obtained and discussed. The studied amidines are characterized by pronounced fluorescence solvatochromism. The results demonstrated that the studied amidine fluorophores have good properties of large Stokes shift, high emission, polarity sensitivity, that offer a great potential for biological imaging.

Keywords: Luminescent dyes; Benzanthrone derivatives; Synthesis; Fluorescence spectroscopy; Solvatochromism

INTRODUCTION

Nowadays luminescent substances have attracted significant attention owing to their opportunities in various functional applications. Organic luminescent materials with bright emission have drawn considerable attention for their wide applications. Despite the significant progress made recently, there is still great potential in the development of luminescent molecular materials, in particular organic highly fluorescent substances. Benzo[a]anthracene-7-one derivatives are polyaromatic hydrophobic substances with useful photophysical properties. Today, luminescent benzanthrone derivatives are used in various fields, such as synthetic and natural fiber dyes, photoconductors, luminophores, fluorescent labels and probes [1-4].

In recent years there has been a growing interest in the design of nitrogen-containing compounds (such as amidines) which can form luminescent complexes and associates in solids and solutions. Compounds with amidine group have played an important role in diverse areas such as catalyst design, material science, medicinal chemistry [5-8].

It is known that substituted aromatic amidines have an intense luminescence in solutions. Furthermore, the use of amidinate-ligated iridium complexes for fabrication of high-efficiency phosphorescent organic light-emitting devices has been reported [9].

Many amidines are employed as versatile tools in numerous applications such as fluorescent turn-on/turn-off sensors for the determination of diverse analytes - metal cations, amines, DNA, etc. [10-13].

For several years our research group has been working on benzanthrone dyes with D-π-A architecture, appearing to be particularly interesting because these dyes ultimately lead to prospective luminescent markers and sensors. In previous works, a series of benzanthrone-substituted amidines were synthesized from the corresponding primary arylamines by their condensation with substituted amides in the presence of phosphorus oxychloride [14-16]. The aim of the present research was to study and compare the photophysical properties of benzanthrone derivatives containing amidine constituents in various positions of the aromatic system.

EXPERIMENTAL

Materials

The studied dyes were synthesized as described in the previous articles [14-16]. The chemical structures of the used compounds are presented in Table 1. The solvents as hexane, chloroform, benzene, ethyl acetate (EtOAc), acetone, ethanol (EtOH), N,N-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) were of spectroscopic grade and were procured from Sigma Aldrich Chemical.

Spectroscopic measurements

Spectral properties of the investigated compounds were measured in various organic solvents with concentrations 10^{-5} M at ambient temperature in 10 mm quartz cuvettes. The absorption spectra were obtained using the UV-visible spectrophotometer Specord`s UV/VIS.

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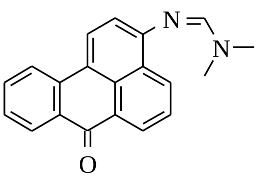
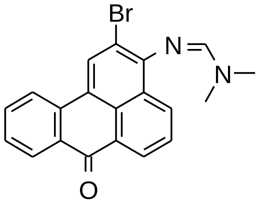
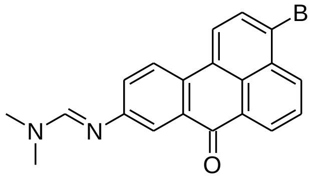
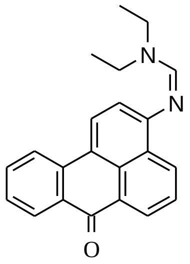
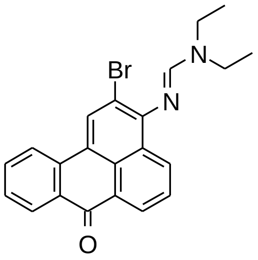
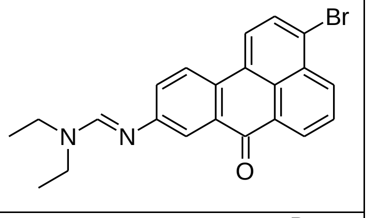
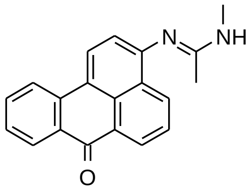
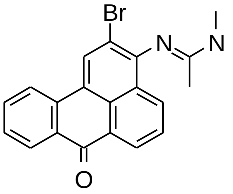
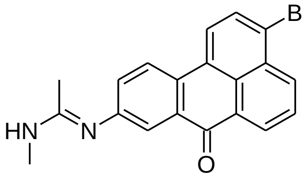
Table 1. Structure of studied amidines.

-A1 	**B1** 	**C1** 
A2 	**B2** 	**C2** 
A3 	**B3** 	**C3** 

The fluorescence emission spectra were recorded on a FLSP920 (Edinburgh Instruments Ltd.) spectrofluorometer using Rhodamine 6G (Φ_0=0.88) as a standard.

RESULTS AND DISCUSSION

In previous studies, benzanthrone derivatives with an amidine group and bromine atom in various position of benzanthrone core were synthesized from the corresponding amino benzanthrones – 3-aminobenzanthrone, 2-bromo-3-aminobenzanthrone and 3-bromo-9-aminobenzanthrone by their condensation with substituted amides in the presence of $POCl_3$. All these substances show pronounced light emission properties.

It was of interest to analyze how different positions of the same constituent affect the optical properties of benzanthrone derivatives, because one of the basic tasks of spectroscopy is to elucidate regularity between chemical structure of a particular substance and its optical characteristics.

In connection with our current interest on the design of novel luminescent compounds for bio-visualization and sensing purposes, we report a comparative study of several new luminescent analogous benzanthrone derivatives. In this work, the spectral data were analyzed for the following compounds:

a) three compounds with an amidine fragment in the 3rd position of the benzanthrone aromatic system (A1-A3);

b) three substances with an amidine group in the 3rd and a bromine atom in the 2nd position of benzanthrone (B1-B3);

c) three compounds with an amidine group in the 9th position and a bromine atom in the 3rd position of the aromatic core (C1-C3).

These luminescent compounds contain a strong electron-donating amidine group and an electron-accepting carbonyl group linked by an aromatic spacer. In addition, the bromine atom affects the electronic density in compounds B1-B3 and C1-C3.

The electronic absorption spectra of the studied compounds (see Table 2) show a broad long-wave band around 420-490 nm, which has a charge transfer character, due to π–>π* electron transfer during the S_0–>S_1 transition [17]. The charge transfer in benzanthrone dyes occurs from the electron donor-acceptor interaction between electron-donating substituents and the electron-accepting carbonyl group of the chromophorous system.

Table 2. Absorption maxima (log e) of the studied amidines in various solvents (concentrations 10^{-5} M).

	A1	A2	A3	B1	B2	B3	C1	C2	C3
Hexane	437 (4.28)	443 (4.35)	432 (3.96)	429 (4.11)	434 (4.03)	427 (4.30)	439 (4.35)	444 (4.45)	433 (4.21)
Benzene	456 (4.27)	461 (4.31)	447 (3.91)	447 (4.02)	448 (4.05)	443 (4.28)	460 (4.38)	461 (4.46)	448 (4.33)
$CHCl_3$	464 (4.18)	460 (4.25)	448 (4.11)	447 (4.06)	449 (4.07)	446 (4.35)	465 (4.37)	472 (4.48)	455 (4.17)
EtOAc	459 (4.22)	465 (4.30)	449 (4.11)	447 (4.00)	448 (4.08)	446 (4.30)	464 (4.38)	466 (4.51)	457 (4.31)
Acetone	462 (4.20)	474 (4.24)	449 (4.06)	448 (4.06)	455 (4.10)	448 (4.36)	473 (4.37)	476 (4.52)	463 (4.30)
Ethanol	471 (4.12)	476 (4.12)	448 (4.07)	447 (3.96)	448 (4.02)	446 (4.34)	473 (4.33)	477 (4.05)	455 (4.24)
DMF	479 (4.30)	484 (4.31)	467 (4.14)	457 (4.03)	462 (4.04)	456 (4.27)	482 (4.30)	485 (4.49)	472 (4.29)
DMSO	488 (4.31)	491 (4.35)	473 (4.13)	462 (3.99)	464 (4.00)	460 (4.26)	490 (4.24)	492 (4.49)	476 (4.34)

Table 3. Fluorescence maxima (quantum yield) of the studied amidines in various solvents (concentrations 10^{-5} M).

	A1	A2	A3	B1	B2	B3	C1	C2	C3
Hexane	528 (0.64)	532 (0.70)	525 (0.64)	523 (0.23)	523 (0.25)	519 (0.29)	504; 527; 554	507; 532; 554	527 (0.18)
Benzene	550 (0.67)	556 (0.74)	565 (0.60)	560 (0.20)	562 (0.22)	565 (0.31)	(0.28) 588	0.27) 594	570 (0.42)
$CHCl_3$	590 (0.56)	615 (0.72)	608 (0.58)	594 (0.25)	601 (0.27)	608 (0.30)	(0.34) 585	(0.32) 584	610 (0.32)
EtOAc	586 (0.62)	586 (0.72)	596 (0.49)	577 (0.23)	582 (0.22)	584 (0.19)	(0.38) 612	(0.37) 608	593 (0.38)
Acetone	608 (0.56)	603 (0.65)	644 (0.57)	606 (0.15)	614 (0.14)	622 (0.15)	(0.29) 657	(0.30) 657	622 (0.34)
Ethanol	646 (0.27)	655 (0.30)	665 (0.18)	624 (0.01)	633 (0.01)	666 (0.05)	(0.10) 621	(0.12) 621	668 (0.14)
DMF	624 (0.33)	615 (0.41)	636 (0.44)	628 (0.03)	622 (0.02)	632 (0.03)	(0.23) 651	(0.20) 634	637 (0.30)
DMSO	632 (0.20)	635 (0.28)	644 (0.48)	659 (0.03)	644 (0.03)	654 (0.03)	(0.12)	(0.11)	648 (0.26)

Table 4. Stokes shifts (in cm^{-1}) of fluorescence maxima of the studied derivatives in various solvents.

	A1	A2	A3	B1	B2	B3	C1	C2	C3
Hexane	3944	3776	4100	4190	3922	4151	3804	3726	4120
Benzene	3747	3706	4672	4514	4527	4874	3688	3641	4777
$CHCl_3$	4602	5479	5874	5536	5633	5975	4498	4351	5585
EtOAc	4721	4440	5493	5040	5139	5299	4458	4336	5019
Acetone	5198	4514	6744	5819	5691	6244	4802	4561	5521
Ethanol	5751	5741	7283	6345	6523	7407	5921	5743	7008
DMF	4851	4401	5690	5958	5568	6107	4644	4516	5487
DMSO	4669	4619	5614	6470	6024	6448	5047	4552	5576

Compounds with only substituted amidine group at 3rd position absorb at 430-490 nm with high extinction coefficients, and emit at 530-650 nm showing both absorption and fluorescence solvatochromism. The introduction of bromine atom to 2nd position was found to cause a blue-shift (10-25 nm) of the absorption and emission bands and decrease in the fluorescent quantum yield. Compounds with bromine atom in 9th position show a red shift of absorption maxima and increase of emission yield in comparison with the derivatives B1-B3.

All amidines are fluorescent in solutions in the region of 520-670 nm (see Table 3) and display large bathochromic shifts (110-150 nm) from hexane to ethanol solutions. However, compounds without a bromine atom in the molecule have a higher quantum yield of radiation (up to 74% in a benzene solution). A large decrease in the quantum yield of radiation for compounds B1-B3 and C1-C3 indicates the energy loss in the excited state due to vibrational relaxation. The interaction of electrons of the bromine atom with the benzanthrone ring probably ensures nonradiative deactivation.

The Stokes shift was calculated because it is an important characteristic for fluorescent compounds. This parameter indicates the differences in the properties and structure of the emitting compound between the ground and the first excited state. Investigated derivatives display a significant Stokes shift (see Table 4), especially large in polar solvents (5700 - 7400 cm^{-1}). This is because the intramolecular charge-transfer effect leads to a large dipole moment in the excited state. Once excited, the solvent molecules surrounding the emitting compound molecule can reorder, resulting in a more stabilized, lower energy excited state. In a polar solvent the conformation of the dye molecule is probably twisted, and the twisted intramolecular charge transfer state (TICT) originates, which red shifts and decreases the efficiency of luminescence [18]. Therefore, the bathochromic shift and weakening of emission with growing solvent polarity might be caused by TICT formation.

Comparing amidines, a large Stokes shift is observed for compounds B1-B3 (up to 7400 cm^{-1} for amidine B3 in ethanol solution), which indicates great polarization of the molecule due to the influence of the bromine atom in 2nd position.

Therefore, the studied amidines exhibit remarkable Stokes shifts, which could minimize self-absorption and provide better fluorescence imaging in biology [19].

CONCLUSION

New data have been obtained on the relationship between the chemical structure of benzanthrone amidines and their photophysical properties, which may be of importance for the development of effective fluorescent derivatives based on the benzanthrone core and can be later used to create new promising fluorescent materials. Performed research demonstrates that the studied amidine fluorophores have good properties of significant Stokes shift, large extinction coefficient, high emission, polarity sensitivity.

The obtained results testify that the fluorescence of the synthesized amidino derivatives is sensitive to the change in polarity of surrounding medium, and fluorescence in the red region (above 600 nm in polar solvents) of the spectrum contributes to a high analytical sensitivity of the method using these fluorophores. These characteristics of the studied benzanthrone dyes demonstrate their potential as biomedical probes for proteins, lipids, and cells. Such dyes can be also utilized as suitable sensing probes for checking solvent polarity.

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