Scientific Journal of Riga Technical University
Material Science and Applied Chemistry

2011
Volume 23

Novel Benzanthrone Dyes: Synthesis and Comparison of Luminescent Properties

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***Abstract.* The presented work focuses on synthesis and comparison of spectroscopic properties of new fluorescent dyes - benzanthrone derivatives containing substituted amino, azo, imino or amidino groups at the 3-position, which show different luminescence characteristics. The spectroscopic behaviour of the obtained substances depends on the polarity of medium, namely their spectral position of absorption and emission, fluorescence intensity demonstrate distinct behaviour in different solvents. Many compounds show a strong fluorescent solvatochromism and a large Stoke's shift.**

***Keywords:* benzanthrone, fluorescent dyes, solvatochromism**

INTRODUCTION

Modern fluorescent technology has a large practical significance in solving many problems of science, medicine and industry. In this connection intensive investigations have been developed for obtaining new fluorescent dyes. The aim of our work is to synthesize new nitrogen-containing derivatives of benzanthrone in order to find perspective luminescent substances.

Benzo[de]anthracen-7-one and its derivatives have been investigated because of the wide range of their applications. Benzanthrone dyes are well known as organic luminophores that emit in the spectral region from green to red. Because of their bright fluorescence, excellent colour characteristics, and high thermo and photostability benzanthrone dyes are used as disperse dyes for textiles and polymers, daylight fluorescent pigments and laser dyes [1,2].

Such derivative as 3-methoxybenzanthrone (MBA) is well known as a hydrophobic fluorescent probe for the investigation of cell membrane micro-viscosity and fluidity [3], conformational changes of proteins [4], and for DNA binding studies [5]. The usefulness of MBA results from a marked sensitivity of its fluorescence parameters to the properties of environment, whereas MBA has a high cytotoxicity for living cells. The replacement of the methoxy group by N-containing groups probably can reduce cytotoxicity.

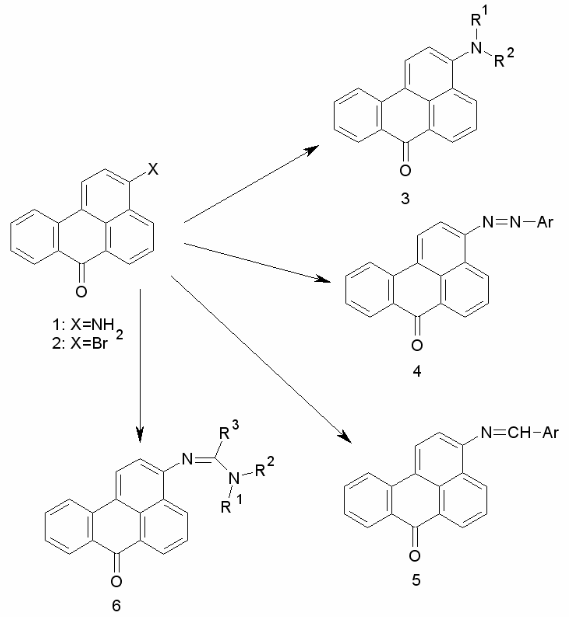
Although some benzanthrone derivatives are currently extensively applied as fluorescent dyes and probes, nitrogen-containing derivatives of benzanthrone are comparatively poorly investigated.

One of the objectives set for achieving the aim is to elaborate methods for synthesis of benzanthrone 3-N-derivatives, i.e. amino, azo, imino and amidino derivatives (compounds 3, 4, 5 and 6 according to Fig. 1) from 3-aminobenzanthrone (1) or 3-bromobenzanthrone (2). Another objective is to study physical and chemical properties of the obtained products in order to investigate relationships between the structure and fluorescent properties of the obtained compounds and their potential use for the purposes of fluorescent analysis.

RESULTS AND DISCUSSION

Benzanthrone 3-aminoderivatives

For synthesis of benzanthrone 3-aminoderivatives (3), two synthetic routes were used. In the first procedure, alkylation reactions of 3-aminobenzanthrone (1) [6] were used.



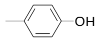
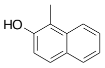
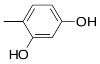
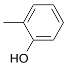
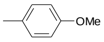
Compound	Ar	R^1	R^2	R^3
3a	-	-$(CH_2)_5$-		-
3b	-	-$(CH_2)_4$-		-
3c	-	H	CH_2Ph	-
4a		-	-	-
4b		-	-	-
4c		-	-	-
5a	Ph	-	-	-
5b		-	-	-
5c		-	-	-
6a	-	Me	Me	Me
6b	-	Me	Me	H
6c	-	Et	Et	Me

Fig. 1. The structure of investigated 3-N-derivatives of benzo[de]anthracen-7-one.

It was found out that 3-aminobenzanthrone in alkylation reactions was not active enough and the attempts to carry out alkylation with 2-chloroethanol, bromocyclohexane, 1-bromopropane and 1-bromobutane failed. Benzylation of amine 1 was carried out by benzylchloride in the presence of a base. The obtained new amino derivative 3c was a violet compound with a bright fluorescence from orange to violet in organic solvents.

The second route for the synthesis of new 3-aminoderivatives of benzanthrone was the nucleophilic substitution reactions of bromo atom on 3-bromobenzanthrone (2)**.** A series of derivatives containing heterocyclic and other moiety was synthesized in this way in our previous works [7,8]. The synthesized dyes had a strong fluorescence in solution and some of them also as crystals, e.g. 3-piperidinobenzanthrone (3a) had a vivid orange luminescence in both crystalline state and in organic solvents.

Photophysical properties of 3-substituted benzanthrones are basically related to the polarisation of the benzanthrone molecule [9]. The polarisation occurring upon irradiation results from the electron donor-acceptor interaction between the electron-donating substituents at the 3-position and the electron-accepting carbonyl group of the chromophorous system (Fig.2). Absorption and emission bands of the dyes largely depend on the electron-donating power of the substituents at the 3-position.

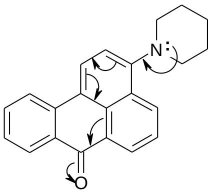


Fig. 2. The path of the charge transfer in the molecule of 3-piperidinobenzanthrone (3a)

Spectral properties of the benzanthrone dyes also depend on the nature of environment because these compounds are environment-sensitive luminescent dyes that display sensitivity to the physicochemical properties of the local environment [8,10]. Environment-sensitive fluorophores are extensively used for the development of new chemosensing materials for molecules and ions [11-13].

All investigated amino derivatives are highly fluorescent compounds with the absorption maximum of about 450-480 nm and the fluorescence maximum – 600-650 nm (Table 1). The fluorescence spectrum of the obtained compounds reveals a positive solvatochromism when going from non-polar benzene to polar ethanol. This behavior is typical of the intramolecular charge transfer character of the exited state. A large wavelength shift of the fluorescence spectrum results from solvent relaxation during the excited-state lifetime caused by an essential change of the probe dipole moment after excitation. On the other hand, absorption maxima of the obtained substances are almost independent of the solvent polarity. The maximum values of batochromic shifts are 15 nm for the absorption spectra and 77 nm for the fluorescence ones.

The Stoke's shift is an important characteristic of fluorescent compounds. It is a parameter which indicates the difference between the properties and the structure of the fluorophores in the ground state and those in the first excited state. It was found out that Stoke's shift values for dyes are significantly large (100-200 nm). When a probe binds in a biological matrix, it enters into a less polar and more viscose environment as compared to the buffer. Therefore all fluorescence characteristics more or less change. Similar phenomena occur when adding the obtained compounds to biomolecules, thus evidencing their binding with the latter. In the presence of biomolecules, emission maximum of all studied amino derivatives 3, shifts to the short-wavelength region up to 37 nm for albumin, and 44 nm for liposomes. Fluorescence parameters of some prepared amino dyes binding them with human serum albumin, model liposomes and living cells were discussed in more details in the previous work [14].

TABLE 1

FLUORESCENT PROPERTIES OF BENZANTHRONE 3-N-DERIVATIVES

Compound	Solvent	λ_{ex} nm	λ_{fl} nm	I_{fl} a.u.
3-amino derivatives (3a-c)	C_6H_6	500-590	580-620	5.5-9.5
	EtOH	470-620	650-670	1.0-3.2
3-imino derivatives (5a-c)	C_6H_6	480-500	570-590	0.1-0.2
	EtOH	490-520	620-650	0.3-0.5
3-amidino derivatives (6a-c)	C_6H_6	450-470	590-630	8.0-12.0
	EtOH	460-520	640-680	7.5-10.0

Though tests of cytotoxicity for the obtained derivatives have not yet been carried out, our data from the experiments with lymphocytes witness that amino dyes have lower cytotoxicity than MBA. It is known that MBA destroys cells after a short period of time (few minutes) [3], but in the presence of amino derivatives 3 lymphocytes remain alive for at least 1 hour.

Diazotation and azo coupling in 3-aminobenzanthrone

The known benzanthrone azo derivatives with azo groups in 3- and 9-positions are deeply coloured dyes for textile fibres. The photoconductor properties of these compounds were recently found and they began to be used as photoreceptors in electrophotographic apparatus and electroluminescent devices [15,16]. Since benzanthrone 3-azoderivatives were not enough described in literature, it was decided to investigate possibilities of synthesis and properties of benzanthrone derivatives with azo group in the 3-position.

A yellow solution of arenediazonium salt was prepared by diazotation of 3-aminobenzanthrone in concentrated hydrochloric acid. The azo coupling reactions were carried out with phenol, resorcinol, 1-naphtol and 2-naphtol. A mixture of two compounds was obtained from 1-naphtol; this mixture proved to be unseparable because of similar solubility of the obtained compounds. In ^{1}H NMR spectra of the obtained azo compounds signals of phenol group protons were observed at 10.48, 11.91 and 17.34 ppm for phenol, resorcinol and 2-naphtol derivatives respectively.

As many other azo dyes, the newly synthesized azo derivatives 4 are non-luminescent compounds, but have interesting colour characteristics, namely azo derivatives are black or dark-green dyes having violet colour in conc. sulphuric acid, blue colour in alkaline ethanol solution and reddish after acid addition. The dyes have strong absorption bands on 360-410 nm, 540-590 nm and 730-750 nm (in DMF and ethanol). It was found that absorption bands of the prepared azo dyes are pH-sensitive. Thus azo derivative 4a at pH 3 has absorption maxima at 591 nm (yellow solution), and at pH 9 – at 408 and 513 nm (red). Aqueous solution of the azo dye 4c shows three changes of colour: from yellow to red at pH 5.8, from red to violet at pH 12.2, and from violet to blue at pH 13.0.

Similar phenomenon was revealed earlier for benzanthrone amide derivative [11]. Authors suggest that dye colour changes at different pH due to the deprotonation of the amide group followed by restoring the internal charge transfer and significant red shift of the absorption maximum in the range of pH 10.50–12.50

Due to their optical properties depending on pH of medium, these new azo dyes can be used for the development of simple colorimetric pH-sensors.

Benzanthrone 3-imino derivatives

Having in mind the experience in synthesis of benzanthrone amino and azo dyes, it was interesting to synthesize new imino derivatives by introducing azomethine group into benzanthrone molecule, which extends the system of conjugated double bonds of the benzanthrone residue thus increasing the chromophore length. As a result, substances with new luminescent properties can be obtained.

This approach was implemented by heating 3-aminobenzanthrone with a series of aromatic aldehydes. In such a way new azomethines 5a-c were obtained with 48-74% yields as crystalline compounds from yellow to brown [17]. Some of them have low stability in water-containing medium undergoing hydrolysis that produces initial amine. This property is an essential disadvantage for using imines as fluorescent probes for biomolecules investigation in water environments. Furthermore, these dyes have yellow fluorescence with low intensity (Table 1).

In the works [18-20] it has been shown that some azomethines 5 have the potential of dyes for liquid crystals and polymer materials, as well as for the synthesis of charge-transfer complexes [21].

Benzanthrone 3-amidino derivatives

Bearing in mind the above mentioned investigations and the marked luminescent properties of the known aromatic amidines [22], a new approach to structural modifications of benzanthrone dyes was started by introducing amidino group into benzanthrone moiety in our previous work [23].

Derivatives 6a-c were obtained with high yields (95-97%) from 3-aminobenzanthrone in reaction with some N,N-substituted amides in the presence of phosphorus oxychloride. The prepared amidine derivatives were crystalline compounds colored from yellow to deep red with absorption maxima at 460-470 nm. The emission maximum of novel compounds remarkably depended upon solvents: in benzene fluorescence maxima was located at 610-615 nm, and in ethanol at 640-680 nm.

These dyes were strongly fluorescent in solutions and displayed large bathochromic shifts (45-60 nm) from chloroform to ethanol solutions with regard to the amino derivatives, for which this shift was 25-40 nm [8]. In benzene fluorescence maxima were located at 610-615 nm, and in ethanol at 655-680 nm. All prepared amidines showed a hypsochromic shift of emission maxima in chloroform solutions in comparison with amine 1. Synthesized fluorophores displayed significant Stoke’s shifts (up to 6900 cm^{-1}) similarly to substituted amino derivatives [8].

The fluorescent properties of some synthesized amidines in the presence of transition metal ions were investigated. The studied amidines showed different spectroscopic behavior in the complex formation process with different metal ions. The dyes underwent fluorescence quenching upon binding with Cu^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+} ions. Such fluorescence quenching of organic fluorophores by heavy metal ions is a well known phenomenon caused mainly by the electron transfer from the excited molecule to the cation, when metal uses its incomplete d orbitals to form a charge-transfer complex with the ligand [13,24]. Further investigations into this phenomenon led to the development of fluorescent chemosensor for detection of environment pollution by transition metal cations.

EXPERIMENTAL

General

The progress of the chemical reactions and the purity of products were monitored by TLC on silica gel plates (Fluka F60254, 20*10, 0.2 mm, ready-to-use), using C_6H_6-CH_3CN (6:1) as eluent. Column chromatography on silica gel was carried out on Merck Kieselgel (230-240 mesh) with benzene as eluent. All melting points were measured on a Kofler apparatus and were uncorrected. IR spectra were recorded on a Specord M80 IR Spectrophotometer using KBr pellets. ^1H NMR spectra were recorded on Bruker equipment, operating at 300 MHz in $CDCl_3$ or DMSO-d_6 (with TMS as internal standard) at ambient temperature. ^{13}C NMR spectra were run in the same instrument at 75.4 MHz using the solvent peak as internal reference.

Commercially available reagents were used without further purification unless otherwise stated.

3-Aminobenzanthrone (1) was prepared by nitration of benzanthrone and following reduction of the obtained 3-nitroderivative according to the literature procedure [23].

Technical 3-bromobenzanthrone (2) was purchased from Across and purified by recrystallization from N,N-dimethylformamide.

Synthesis of 3-amino derivatives of benzanthrone (3a-c)

Procedure A: by alkylation of 3-aminobenzanthrone (1).

3-Benzylaminobenzanthrone 3c**.** Mixture of amine 1 (0.55 g; 2.2 mmol), benzylchloride (0.5 ml; 4.4 mmol) and K_2CO_3 (0.3 g; 2.2 mmol) was heated for 4 h at 150^0C. After cooling, filtering and column chromatography violet compound (0.26 g; 35%) was obtained. M.p.=183-184^0C. UV [$CHCl_3$, nm (lgε)]: λ=278 (6.42); 395 (6.01); 410 (6.03); 498 (5.98). IR (KBr; cm^{-1}): ν=1568 (C=C); 1668 (C=O); 2860, 2928, 3039 (C-H), 3388 (N-H). ^1H NMR (DMSO-d_6, ppm): δ=4.63 (d, 2H, CH_2); 6.60 (d, 1H, NH); 7.23 – 8.87 (m, 14H, CH_{arom}). Found, %: C 84.41; H 4.80; N 4.01. $C_{24}H_{17}NO$. Calculated, %: C 85.95; H 5.11; N 4.18.

Procedure B: by nucleophilic substitution of bromo atom in 3-bromobenzanthrone (2) in reactions with some amino compounds described in our previous works [7,8].

Synthesis of 3-azo derivatives of benzanthrone (4a-c)

Diazotation. The amine 1 (5 mmol) was dissolved in 6 N HCl (15-20 ml). The mixture was cooled by means of an ice-water bath and aqueous solution of $NaNO_2$ (15%, 4 ml) was added dropwise for 15 min. The resulting yellow solution was stirred at that temperature for 1 h. The excess of HNO_2 was destroyed by adding solid urea (0.3 g).

Coupling. The prepared solution was added to a solution of the appropriate hydroxyaryl compound (5 mmolol) in aqueous NaOH solution (10%; 7 ml) at 3-5^{0}C with vigorous stirring. After stirring for 1 h, the mixture was neutralized by adding 2 N HCl (10 ml). The precipitated dye was isolated by filtration and washed with water (2*20 ml) and ethanol (2*10 ml). Purification was achieved by recrystallization using solvents given below.

3-(4-Oxyphenyl)azobenzanthrone (4a). The amine 1 (1.23 g; 5 mmol) was diazotised and the salt was coupled with phenol (0.47 g; 5 mmol). The obtained product was purified by recrystallization from acetone which produced a dark-brown compound (0.98 g; 57%).M.p.=281-283°C. UV [DMF, nm (lgε)]: λ=284.1 (4.13); 449.7 (4.40). IR (KBr; cm^{-1}): ν=1504 (N=N); 1566 (C=C); 1640 (C=O); 2928 (C-H); 3300 (O-H). ^{1}H NMR (DMSO-d_6, ppm): δ=7.07 – 9.33 (m, 13H, CH_{arom}); 10.48 (s, 1H, OH). Found, %: C 78.30; H 4.10; N 7.67. $C_{23}H_{14}N_2O_2$. Calculated, %: C 78.84; H 4.03; N 8.00.

3-(2-Oxynaphthyl-1)azobenzanthrone (4b). The amine 1 (1.23 g; 5 mmol) was diazotised and the salt was coupled with 2-naphthol (0.72 g; 5 mmol). The obtained product was purified by recrystallization from DMF which produced a black compound (1.24 g; 63%).M.p.=278-279°C. UV [DMF, nm (lgε)]: λ=284.1 (4.28); 545.9 (4.51). IR (KBr; cm^{-1}): ν=1502 (N=N); 1580 (C=C); 1654 (C=O); 2924 (C-H); 3400 (O-H). ^{1}H NMR (DMSO-d_6, ppm): δ=6.90 – 8.91 (m, 15H, CH_{arom}); 17.34 (s, 1H, OH). Found, %: C 80.46; H 4.09; N 6.85. $C_{27}H_{16}N_2O_2$. Calculated, %: C 80.99; H 4.03; N 7.00.

3-(2,4-Dioxyphenyl)azobenzanthrone (4c). The amine 1 (1.23 g; 5 mmol) was diazotised and the salt was coupled with resorcinol (0.55 g; 5 mmol). The obtained product was purified by recrystallization from DMF which produced a dark-green compound (1.08 g; 60%).M.p.=310°C. UV [DMF, nm (lgε)]: λ=284.8 (4.25); 550.8 (4.38). IR (KBr; cm^{-1}): ν=1501 (N=N); 1572 (C=C); 1650 (C=O); 2924 (C-H); 3350 (O-H). ^{1}H NMR (DMSO-d_6, ppm): δ=7.63 – 9.17 (m, 12H, CH_{arom}); 11.91 (s, 2H, OH). Found, %: C 74.88; H 3.93; N 7.42. $C_{23}H_{14}N_2O_3$. Calculated, %: C 75.40; H 3.85; N 7.65.

Synthesis of 3-imino derivatives of benzanthrone (5a-c)

The target benzanthrone 3-iminoderivatives (5a-c) investigated in the present study have been synthesized by condensation of amine 1 with corresponding aldehydes as previously described [17].

Synthesis of 3-amidino derivatives of benzanthrone (6a-c)

The investigated benzanthrone 3-amidinoderivatives (5a-c) have been synthesized by condensation of amine 1 with corresponding amides in the presence of phosphorus oxychloride using method described in our previous work [23].

Spectroscopic measurements

Spectral properties of the investigated compounds were measured in benzene, chloroform and ethanol with concentrations 10^{-5} M at room temperature in 10 mm quartz cuvettes. All solvents were of p.a. or analytical grade. The absorption spectra were obtained using a UV-visible spectrophotometer "Specord`s UV/VIS". The fluorescence emission spectra were recorded using spectrofluorimeter Spectrofluo JY3 (ISA Jobin Yvon Instruments S. A).

CONCLUSIONS

In the present work, synthetic methods for preparing new benzanthrone 3-aminoderivatives were discussed such as alkylation of 3-aminobenzanthrone and nucleophilic substitution of bromo atom in 3-bromobenzanthrone. Synthesis of new benzanthrone azo and imino derivatives from 3-aminobenzanthrone was reviewed, as well as preparation of new highly luminescent 3-amidino derivatives was described.

It was demonstrated that various nitrogen-containing derivatives of benzanthrone have differing luminescent properties: the obtained azo derivatives are not luminescent, synthesized imines with some exception do not have luminescent properties either, whereas amino and amidino derivatives show significant fluorescence the parameters of which depend on structure of the substance.

The achieved results testify that fluorescence of amino and amidino derivatives are sensitive to the changes of the medium polarity. Fluorescence in the red region of spectrum contributes to the high analytical sensitivity of the method. It was shown that most obtained compounds meet the requirements for the substances as potential fluorescent probes, which provides wide possibilities for the use of these compounds. So in addition to such widely used probes as lipophylic fluoresceins, lipophylic coumarins, laurdan, and MBA, the drophobic dyes described in the present artice are offered for the use in membrane investigation. Due to their properties, these potential fluorescent probes can have a wide range of applications, particularly for the determination of micropolarity of complex macromolecules.

ACKNOWLEDGEMENTS

The study has been supported by EU Structural Funds project Nr 2009/0205/1DP/1.1.1.2.0/09/APIA/VIAA/152

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Jelena Kirilova, Irena Ivanova. Jaunas benzantrona krāsvielas: sintēze un luminiscento īpašību salīdzināšana

Darbā ir aplūkotas jaunu slāpekļa saturošu 3-aizvietotu benzantrona atvasinājumu iegūšanas metodes, to skaitā amīnu, imīnu, amidīnu un azoatvasinājumu sintēze. 3-aminoatvasinājumu iegūšanai bija izmantotas divas pieejas: 3-aminobenzantrona alkilēšanas reakcijas un broma atoma nukleofilās aizvietošanas reakcijas 3-brombenzantronā. Sintezētiem amīniem piemīt intensīva luminiscence šķīdumos, bet dažiem arī kondensētā stāvoklī. Šķīdumos aplūkotie aminoatvasinājumi izrāda izteiktu solvatohromiju – pieaugot šķīdinātāja polaritātei, luminiscences joslas batohromi pārbīdās. Ņemot vērā luminiscences parametru tiešo atkarību no vides polaritātes, iegūtos savienojumus var uzskatīt par potenciālām fluorescentām zondēm. Darbā aprakstītas jaunas benzantrona azokrāsvielas, kuru iegūšanai bija izmantota 3-aminobenzantrona diazotēšanas reakcija ar sekojošu azosametināšanu ar fenolu, rezorcīnu un naftoliem. Izpētītas iegūto azosavienojumu optiskās īpašības, ir parādīts, ka sintezētām azokrāsvielām piemīt pH-indikatoru īpašības: krāsu pārejas novērojamas vāji skābā un sārmainā vidē. 3-Iminoatvasinājumu iegūšanai izmantota 3-aminobenzantrona kondensācijas reakcija ar aromātiskajiem aldehīdiem. Ir parādīts, ka sintezētie azometīni ir nestabili ūdens vidē un savienojumi ar zemas intensitātes luminiscenci, kas ierobežo to izmantošanu kā fluorescentas zondes bioloģisko objektu pētījumos. Atšķirībā no imīniem apskatītie amidinoatvasinājumi ir krāsvielas ar izteiktām luminiscentām īpašībām. Ir atrasts, ka pārejas metālu jonu klātbūtnē novērojama amidīnu šķīdumu luminiscences dzēšana, ko turpmāk var izmantot jaunu pārejas metālu jonu sensoru izstrādei. Aplūkotais materiāls liecina par to, ka benzantrona atvasinājumu vidū var atrast jaunus perspektīvus luminoforus ar plašām izmantošanas iespējām.

Елена Кирилова, Ирена Иванова. Новые бензантроновые красители: синтез и сравнение люминесцентных свойств

В работе рассмотрены способы получения ряда новых азотсодержащих 3-замещенных производных бензантрона – аминов, иминов, амидинов и азопроизводных. Для получения 3-аминопроизводных использовались два подхода: алкилирование 3-аминобензантрона и реакция нуклеофильного замещения атома брома в 3-бромбензантроне. Полученные амины характеризуются интенсивной люминесценцией в растворах, а некоторые из них и в твердом состоянии. Для растворов рассматриваемых аминов наблюдается ярко выраженная сольватохромия - с увеличением полярности растворителя, происходит батохромный сдвиг полос люминесценции. Учитывая зависимость параметров люминесценции аминопроизводных от полярности окружающей среды, полученные вещества можно рассматривать как потенциальные флюоресцентные зонды. В работе описаны новые азопроизводные бензантрона, получаемые диазотированием 3-аминобензантрона с последующими реакциями азосочетания с фенолом, резорцином и нафтолами. Изучены оптические свойства синтезированных азокрасителей, в том числе показаны их pH-индикаторные свойства в слабокислой и щелочной среде. Для получения 3-иминопроизводных использовалась реакция конденсации 3-аминобензантрона с ароматическими альдегидами. Синтезированные азометины проявили себя как соединения с низкой интенсивностью люминесценции и нестабильные в водной среде, что существенно ограничивает их применение в исследовании биологических объектов в качестве флуоресцентных зондов. В отличие от них полученные амидины характеризуются ярко выраженными люминесцентными свойствами, кроме того, было выявлено, что в присутствии ионов переходных металлов наблюдается значительное тушение люминесценции в растворах амидинопроизводных, что в дальнейшем может быть использовано для разработки оптических сенсоров на ионы переходных металлов. Таким образом, среди производных бензантрона можно найти перспективные люминофоры с широким спектром полезных свойств.