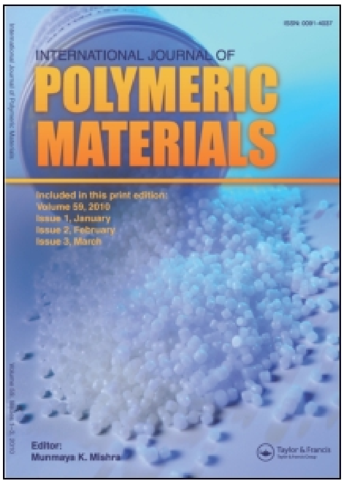

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Synthesis and Photophysical Properties of Azomethynes-Bifluorophores

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The method of the synthesis of unsymmetrical azomethynes-bifluorophores where one of the fluorescent fragments is a donor of electron excitation energy and the second one is an acceptor was worked out. Photophysical properties of azomethynes-bifluorophores were investigated. It was shown that in these compounds non-radiation energy transfer takes place. It was established that quantum-chemical semiempirical method AM1 may be used for the calculation of spatial structure of amines-fluorophores.

Keywords: Absorption; fluorescence; azomethynes-bifluorophores; transfer of electron excitation energy

INTRODUCTION

Large attention of the researchers is currently focussed on, molecules-bifluorophores [1–3], that is connected to wide prospects of their practical application. They can be used in new information and logical systems [4], in molecular electronics [5], as converters of short-wave radiation in long-wave one, for information transfer on optical fibre communication lines [6], as effective scintillators, for new laser environments, for creation of high-power solar batteries *etc.*

Therefore the principal aim of our research is the synthesis of polymers containing two fluorophores in the main polymer chain, where one of them is the donor of energy of electronic excitation, and

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*Corresponding author.

the other-acceptor, study of their spectral-fluorescent characteristics and the opportunity of non-radiation transfer of energy of electronic excitation within the macromolecule. The study of photophysical processes in polymers – bifluorophores during absorbtion of light will allow to establish laws and mechanisms of radiation and non-radiation inside and intermolecular energy transfer and to develop the basis of the management of processes of energy transfer in polymers.

RESULTS AND DISCUSSION

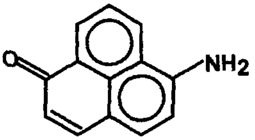
As the object of the research poly(schiff's bases)- bifluorophores were used. Earlier poly(schiff's bases) – fluorophores that containt fluorophores in the main chain were obtained by us for the first time by polycondensation of dialdehydes with diamines-fluorophores. Due to high polymer chain rigidity the solutions of this polymers have the abnormal high for polymers quantum yield of fluorescence reaching 80% at room temperature [7].

Poly(schiff's bases) – bifluorophores were not described earlier. The opportunity of non-radiation energy transfer in poly(schiff's bases) – bifluorophores is determined by that the chromophores – donors and chromophores – acceptors are on rather close distance (about 15 Å), and of conjugation between dialdehydes and amines components of polymer [8].

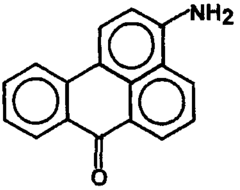
Synthesis of polymers – bifluorophores and the study of the mechanism of electronic excitation energy transfer in polymers are complicated because of specificity of a macromolecule structure. Therefore one of the perspective approaches to the decision of this problem is the development of the method of synthesis of the substances modelling of repeating units of poly(schiff's bases) – bifluorophores and study of the law of energy transfer in them. The received data can be used as the basis for development of methods of synthesis of polymers – bifluorophores and study of the mechanism of energy transfer in such polymers.

Therefore the object of the present stage of investigation was the synthesis of azomethynes-bifluorophores, modelling the elementary unit of poly(schiff's bases) – bifluorophores, and the study of possibility on non-radiation energy transfer in these substances.

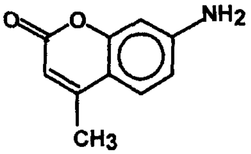
Azomethynes-bifluorophores were obtained by condensation of dialdehyde of terephthalic acid with two monoamines-fluorophores or with mono- and diaminofluorophores. The choice of mono- and diamines-fluorophores was determined by their spectral-fluorescent characteristics, just degree of overlap of the radiation field of the amine – donor of energy of electronic excitation by the field of absorption of energy of amine-acceptor. On the base of literary and experimentally data the following mono- and diamines – fluorophores were chosen:



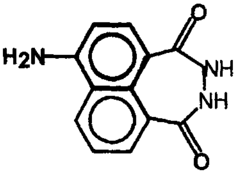
6-amonophenalenone (**1**);



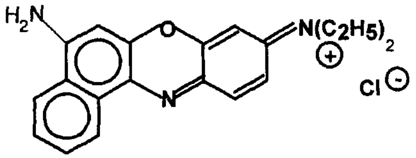
3-aminobenzantron (**2**);



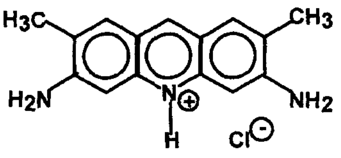
7-amino-4-methylcoumarin (**3**);



4 -amino-1,8- naphthal-
hydrazide (**4**)



5-amine-9-diethylaminebenzo-(a)
phenoxazonium chloride (**5**)



2,8-diamine-3,7-dimethylacrydine
hydrochloride (**6**)

The selection of substances which may be used as components of bifluorophores can be realized on the base of spectral-fluorescent characteristics obtained by experimentally or by using quantum-chemical methods of calculations. Because of this it was necessary to find a special method for calculations of absorption spectra. Therefore, semiempirical quantum-chemical method CNDOL/22 for calculation of absorption electronic spectra was chosen.

The spatial structure of substances **1**–**6** was calculated by semiempirical quantum-chemical method AM1 [9] with full optimization of their geometry. The absorption electronic spectra of these substances was calculated in approximation of the multireference self-consistent field (MR SCF), where only singlet excited states taken into account. The calculation method used was parameterized specially for UV spectra calculations. Ground state correlation energy was approximated by dispertion functional:

$$E_{\text{disp}} = 3/2^{*}i(a)^{*}i(b)^{*}\text{pol}(a)^{*}\text{pol}(b)/(i(a)+i(b))^{*}r(a,b),$$

where $i(a)$, $i(b)$ and pol(a), pol(b) – ionization potential and polarizibilities of atoms a and b, respectively; $r(a, b)$ – interatomic distance. The summation of all contributions listed above has allowed to obtain more precise total energy value of the molecules. The rest of parameters was calculated using known Slater and Helmholz formulas. Molecule **2** possesses high conformational flexibility which is determined by weak conjugation of carbonyl group with the rest π-system of the molecule. Conformational felxibility of **2** was studied by scanning torsion angle C(Ar)—C(Ar)—C(=O)—C(Ar) in the range of ± 40° with an increment of 10° and optimization of the rest geometrical parameters of the molecule at the every point (Tab. I). The absorption spectra of

TABLE I Change of energy (*E* of a molecule (2) at change of torsional angle C(ar)—C(ar)—C(=O)—C(ar)

Torsion angle, degree	ΔE, (*Kkal/mol*)
0	0
10	0.14
20	0.82
30	2.10
40	4.10

molecule **2** were calculated for equilibrium geometry and for non-planar conformation of dihydrocycle. In the calculation following parameters were changed: core repulsion pential, two-electrone integrals calculated by Ono formula; two-center one-electron integrals calculated by Wulfberg and Helmholz formulas. The spectrum obtained at the equilibrium conformation contained inactive long-wave band 531 nm. The same situation was observed for the molecule with torsion angles 10° and 40°. However, in its absorption spectrum with torsion angles 20° and 30° there were active bands at wave lengths 539 and 543 nm, respectively.

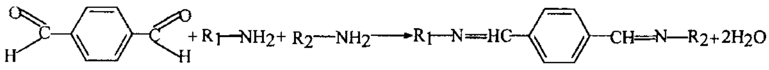
In Table II the results of absorption spectra calculations of all compounds are given. From Table II one can see that the theoretical results are well agreed with experimental ones. The divergence in wave lengths of calculated and experimental maxima of absorption bands does not exceed 20–30 nm. Probably, it is caused by both errors of the calculation technique and strong influence of solvent (*N*-methylopyrrolidone-2) on the spectral bands displacement. As a whole, the study fulfilled has demonstrated an opportunity of the calculation technique usage for bifluorophores components selection.

TABLE II Theoretical and experimental absorption spectra of the solutions of substances **1**–**6** in *N*-methylpyrrolydone-2

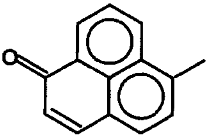
Sus	*Experiment* $\lambda_{abs.}$, *nm*	*Calculation* $\lambda_{abs.}$, *nm*	$\Delta\lambda_{ams.} =$ $\lambda_{theor.} - \lambda_{exp.}$	*E*, l/*mol·cm*
1	290	295	0	
	330	370	1	
	515	539–543	13–17	18600
2	295	361	−1	41600
	369			
	526			
3	362	266	−19	
		463	18	15360
4	285	325	−2	
	445	370	−9	
		511	1	
		545	−21	17000
5	327	285	−25	
	379	390	−11	15600
	510			
	566			
6	310			
	401			

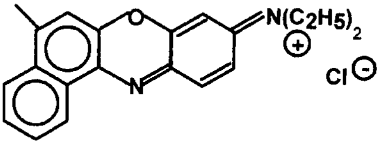
Mono- and diamines, that was chosen as initial substances for synthesis of azomethynes-bifluorophores, considerably differ on reaction ability. It could results in formation of the mixture of azomethynes-fluorophores and azomethynes-bifluorophores during synthesis. Because of this we developed the methods of the selective production of asymmetrical azomethynes-bifluorophores. According to one step method of synthesis the solution of dialdehyde of terephthalic acid in dimethylformamide is gradually added to the mixture of solutions of amines-fluorophores in dimethylformamide at 120°C.

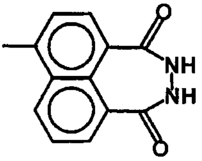
The reaction coursed according the following scheme:



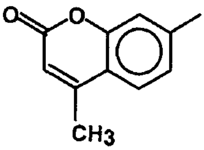
where R_1



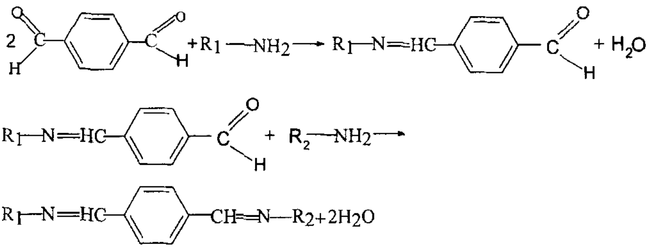




R_2 -



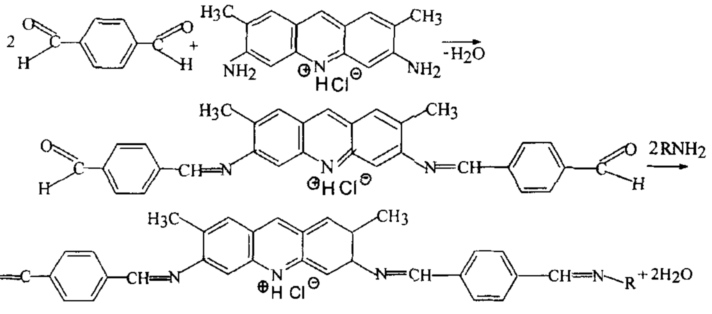
According to the second method azomethynes-bifluorophores have synthesised in two stages. On the first stage the condensation of the monoamine-fluorophore with the surplus of dialdehyde of terephthalic acid is realized. On the second stage azomethyne-fluorophore with the end aldehyde group reacts with second mono-amine.



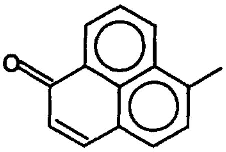
The formulas R1 and R2 are given above.

The study of products of reaction by the method of Thin Layer Chromatography has shown, that with use of the same initial monoamines asymmetrical azomethynes-bifluorophores of an identical structure are formed both with one stage, and with two stage method of synthesis.

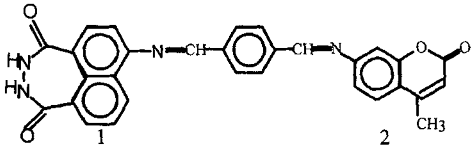
For production of symmetrical azomethynes-bifluorophores dimine-fluorophore is used as one of initial substances. In this case at the first stage of reaction diamine-fluorophore interacts with surplus of dialdehyde of terephthalic acid. On the second stage azomethyne – fluorophore with two end aldehyde groups reacts with the monoamine. For example:



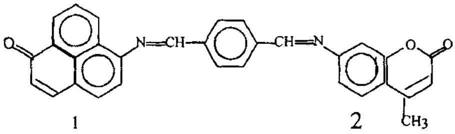
Where R -



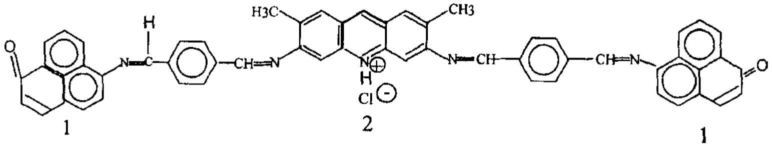
So 5 azomethyne-bifluorophores were synthesised. All of them were synthesised by us for the first time (where 1 – donor of energy 2 – acceptor of energy).



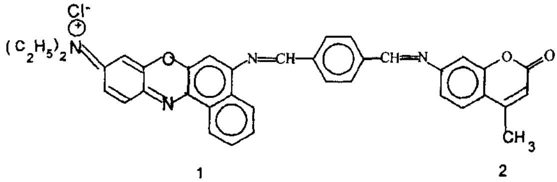
I



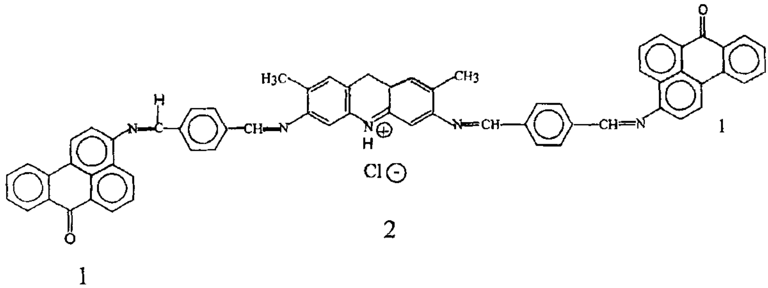
II



III



IY



Y

The individuality of the synthesised substances is confirmed by the date of Thin Layer Chromatography, structure – by the data of the element analysis and UR-spectroscopy.

The presence of non-radiation transfer of the energy of electron excitation was determined by comparison of absorption and radiation spectrums of initial substances and molecule – bifluorophore.

On Figure 1 the spectra of absorption and fluorescence of the solutions of 7-amino-methylcoumarin (**3**), 4-amino-1,8-napthalhydrazide (**4**) (a) and bifluorophore containing this amines (**I**) (b) in *N*-methylpyrrolydone are given. From Figure 1 one can see the significant overlap of fluorescence field of the donor and absorption field of the acceptor of energy. It is shown (Fig. 1b) that there are bends of donor and acceptor of energy at the spectrum of absorption of bifluorophore. That once again confirms a structure of this azomethyne-bifluorophore. In the spectrum of fluorescence of **I** received by excitation at a band of the excitation of donor fragment ($\lambda = 360\,\text{nM}$), the band of fluorescence of acceptor is observed. In unequivocally testifies about non-radiation energy transfer. The presence of the emission band of donor fragment in the spectrum of fluorescence of bifluorophore is connected with incomplete transfer of electronic excitation energy from the donor fragment to the acceptor fragment because the efficiency of the energy transfer is caused not only by the degree of overlap of fluorescence spectra of the donor and adsorption spectra of the acceptor, but also by the distance between them, and their mutual orientation [10].

On Figure 2 the spectra of absorption and fluorescence of bifluorophore **Y** and the initial substances are given. In this case the significant overlap of fluorescence band of the donor and absorption band of acceptor also is observed. In the fluorescence spectrum of bifluorophore, received by excitation at a band of the excitation of donor energy fragment, one can see the band appropriated to fluorescence of acceptor. Thus, for this substance non-radiation energy transfer is observed too.

On Figures 3, 4 the spectral characteristics of the other bifluorophores and initial monoamines-fluorophores are given. As well as in the previous cases, significant overlap of spectral fields of fluorescence of the donor and absorption of acceptor is observed. That testifies about correct selection of the initial fluorophores for synthesis of bifluorophore. In spectrum of fluorescence of bifluorophores received

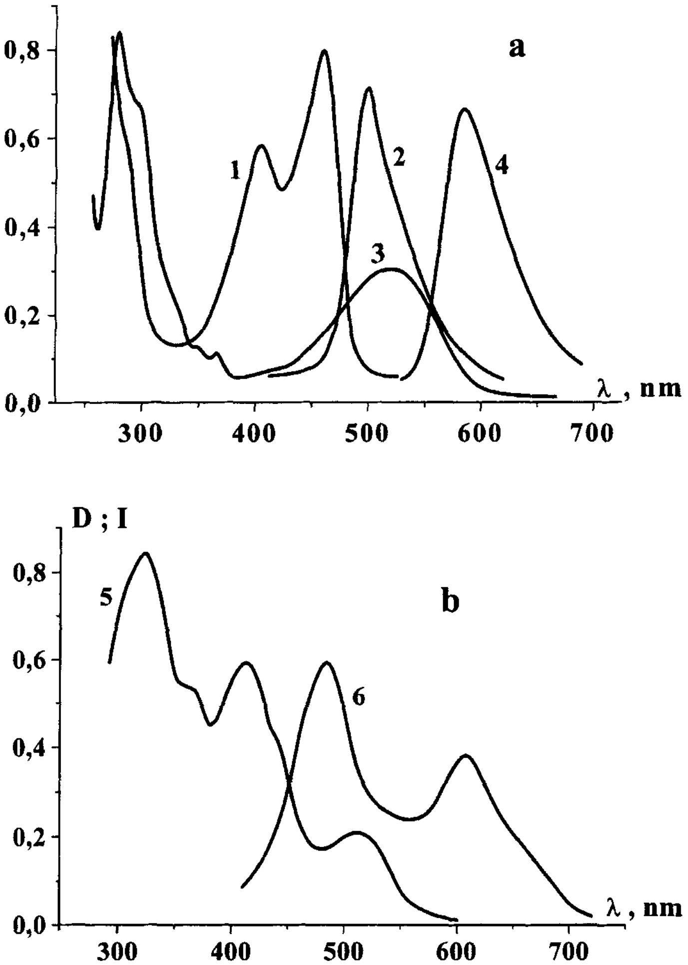


FIGURE 1 Spectra of absorption (1,3,5) and fluorescence (2,4,6) of 2,8-diamine-3,7-di-methylacrydine hydrochloride (1,2), 3-aminobenzantron (3,4) (a) and bifluorophore Y on their basis (5,6) (b).

by excitation at a band of the excitation of donor energy fragment the bands of the acceptor fluorescence are distinctly observed. The spectra of absorption of all azomethynes-bifluorophores are the wide bands with maximums closed to maximums of absorption of initial mono-amines-fluorophores. For all investigated substances the position

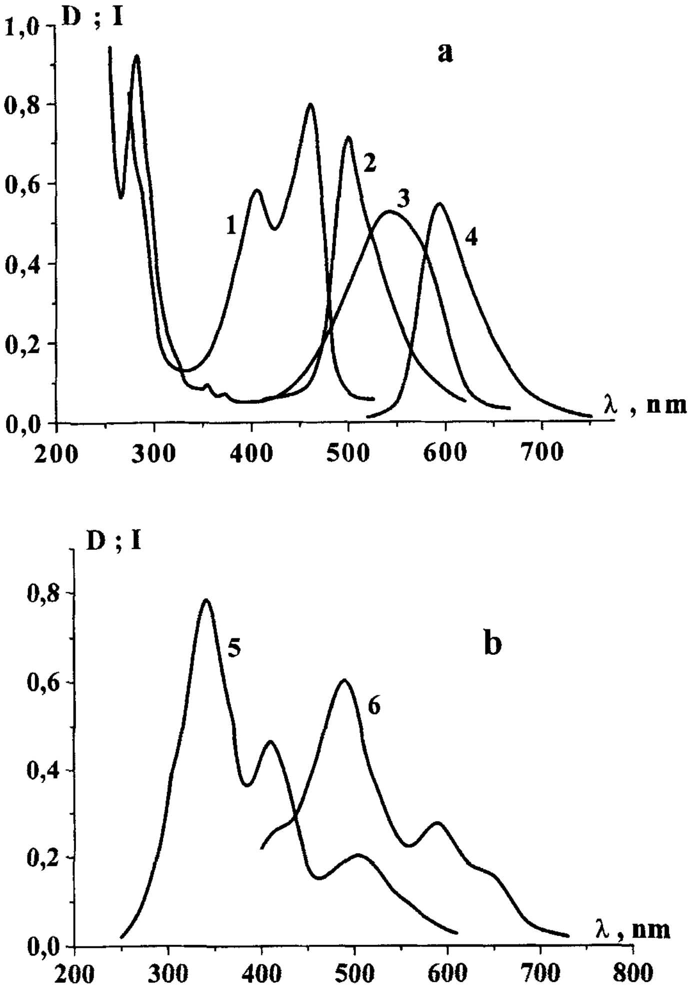


FIGURE 2 Spectra of absorption (1,3,5) and fluorescence (2,4,6) of 2,8-diamine-3,7-di-methylacrydine) hydrochloride (1,2), 6-aminophenalenone (3,4) (a) and bifluorophore III on their basis (5,6) (b).

of maximum of the acceptor absorption band does not depend on its molecular mass or volume of auxochromic group.

In Table III the quantum yields of fluorescence of solutions of initial amines-fluorophores and bifluorophores in *N*-methylopyrrolidone-2

TABLE III Quantum yields of fluorescence of bifluorophores and amines-fluorophores in *N*-methylpyrrolydone-2

Bifluorophore	*Quantum yield of fluorescence*			
	Amine component of bifluorophore		*Bifluorophore*	*Quantum yield of energy transfer*
	Donor of energy	*Acceptor of energy*		
I	0.30	0.42	0.18	0.12
II	0.75	0.42	0.54	0.39
II	0.75	0.69	0.36	0.36
IY	0.47	0.42	0.23	0.15
Y	0.48	0.69	0.37	0.37

*The structures of fluorophores are shown on the pages 10 and 11.

and quantum yield of energy transfer are given. From the table one can see, that the quantum yield of fluorescence of bifluorophores is lower, than quantum yield of initial fluorophores. It means that in the case of bifluorophores there are additional ways of energy dissipation. The losses of energy in this case, apparently, are caused by oscillatory and rotary movements around the bonds in aldehyde fragment of bifluorophore.

The comparison of the degree of overlap of absorption and fluorescence spectrums of the donor and acceptor of energy for all bifluorophores and quantum yield of energy transfer testifies that with the increase of the degree of overlap the quantum yield of energy transfer is increased. Absence of conjugation between chromophores [8] and large distance between them (about 15 Å) [10] exclude the opportunity of energy transfer on the mechanism of internal conversion [11].

Thus for the first time methods of synthesis of asymmetrical and symmetrical azomethynes-bifluorophores are developed and their photophysical properties are investigated. It is established, that in azomethynes-bifluorophores non-radiational transfer of energy of electronic excitation takes place. Non-radiation transfer of energy in azomethynes-bifluorophores can be apparently observed from the viewpoint of dipol-dipol interaction, taking into account the distance between chromophores and direct proportional dependence between a constant of the speed of energy transfer and size of the integral of spectrums overlap [10].

EXPERIMENTAL

Bifluorophore I on a Basis of 7-amino-4-methylcoumarin(3) and 4-amino-1,8-naphthalhydrazide(4) (Two Steps Method of the Synthesis)

1. The Synthesis of Aldehyde-fluorophore

To the solution of 0.55 g (0.0025 mol) 4-amino-1,8-napthalhydrazide (4) in 15 cm^3 of *N*-methylpyrrolydone a solution of 0.67 Γ (0.005 mol) dialdehyde of terephthalic acid in 5 cm^3 of *N*-methylpyrrolydone was added. The reaction mixture was heated under argon at 145–150°C for 6 h. Then the reaction mixture was cooled up to room temperature and poured dropwise into 100 cm^3 of the mixture methanol : water (1 : 4, vol). The precipitated azomethyne-fluorophores with end aldehyde group was filtred off, washed by water, dried in vacuum above $CaCl_2$. The mass of the precipitate was 0.98 Γ.

Found: C – 66.56; H – 4.20; N – 11.11
Calc. for $C_{20}H_{13}N_3O_3 \cdot H_2O$: C – 66.48; H – 4.16; N – 11.63

In UR-spectrum of the substunce the band 1650 cm^{-1} (C=N) and 1714 cm^{-1} (aldehyde group) are observed. There are no bands in the field 3200–3400 cm^{-1} appropriated to free aminogroups.

2. The Synthesis of Azomethyne-bifluorophore

0,25 g (0,00069 mol) of aldehyde-fluorophore was dissolved in 15 cm^3 of DMF in a 50 ml two-necked flaskfitted with a condenser and capillary for argon supply. Solution of 7-amino-4-methylcoumarin (0,12 g, 0,00069 mol) in 5 cm^3 of DMF and 1 cm^3 of *p*-xylol was added. The reaction mixture was heated under argon to 140°C and kept at this temperature for 5 h. Then the mixture was heated to 180°C and 10 cm^3 of DMF was evaporated. After cooling to room temperature the reaction mixture was poured out in methanol. The beads were filtered off, washed with methanol and then dried under vacuum for 12 h. The mass of beads was 0,21 g.

Found: C – 70.74; H – 4.14; N – 11.62
Calc. for $C_{30}H_{20}N_4O_4 \cdot 1/2\ H_2O$: C – 70.73; H – 4.13; N – 11.00
$\lambda_{max}\,cm^{-1}$ 1650 cm^{-1} (C=N) is observed.

Bifluorophore on the Basis of 7-amino-4-methylcoumarin(3) and 6-aminophenalenone(4) (Two Steps Method of the Synthesis)

1. Synthesis of Aldehyde-fluorophore

Dialdehyde of terephthalic acid (4.02 g, 0.03 mol) was dissolved in 150 cm^3 of diethyl ether in a 250 cm^3 two-necked flask fitted with a condenser and capillary for argon supply and heated to 30°C. Solution of 6-minophenalenone (0.9 Г, 0.0046 mol.) was added gradually within 2 hours. Solution kept at this temperature for 2 hours. Then sulphuric ether was evaporated and solution poured out in 200 cm^3 of water. The beads were filtered off, washed with methanol, dried in vacuum for 12 h., recrystallized from isopropyl alcohol and dried in vacuum for 24 h. The mass of beads was 0,21 g.

2. Synthesis of Azomethyne-bifluorophore

Solution of aldehyde-fluorophore (0.31 g, 0.001 mol) in 10 cm^3 of DMF and solution of 7-amino-4-methylcoumarin (0,18 g, 0.001 mol) in 10 cm^3 of DMF and 1 cm^3 of *p*-xylene were placed in two-necked flask fitted with a cdenser and capillary for argon supply, heated to 140°C and kept at this temperature for 5 h. Then 10 cm^3 of DMF was evaporated. After cooling to room temperature solution poured out in methanol. The beads were filtered off, washed with methnol, dried in vacuum for 12 h., recrystallized from isopropyl alcohol and dried in vacuum for 24 h. The mass of beads was 0,29 g.

Found, C – 71.30; H – 4.79; N – 6.14;
Calc. for $C_{31}H_{20}N_2O_3 \cdot 3H_2O$ C – 71.26; H – 4.98; N – 5.36
$\lambda_{max}\,cm^{-1}$ 1650 cm^{-1} (C=N) is observed.

Bifluorophore on the Basis of 7-amino-4-methylcoumarin(3) 5-amine-9-diethylaminebenzo – (a) – Phenoxazonium Chloride (5)

Solution of 7-amino-4-methylcoumarin in 10 cm^3 of DMF and solution of 7-amino-4-methycoumarin (0,18 g, 0.001 mol) in 10 cm^3 of DMF and 1 cm^3 of xylene were placed in two-necked flask fitted with a condenser and capillary for argon supply and heated to 140°C. Solution of dialdehyde of terephthalic acid (0.134 g, 0.001 mol) in 2 cm^3 of *N*-methylpyrrolidone was added gradually within 4 hours. Then the reaction mixture was heated 10 160°C, kept for 3 h., cooled and poured into 50 cm^3 of the mixture methanol : water = 1 : 4, vol.

The beads were filtered off, washed with water, dried in vacuum for 12 h. The mass of beads was 0,25 g.

Found: C – 65.58; H – 5.30; N – 9.00; Cl – 5.23
Calc. for $C_{38}H_{31}N_4O_3Cl \cdot 4H_2O$ C – 65.28; H – 5.58; N – 8.02 Cl – 5.08

Bifluorophore on the Basis 2,8-diamine-3,7-dimethylacrydine Hydrochloride(6) and 6-aminophenalenone(4)

The solution of dialdehyde of terephthalic acid (2.68 g, 0.02 mol) in 15 cm^3 of DMF, 2 cm^3 of xylene and solution of 2,8-diamine-3,7-dimethylacrydine) hydrochloride (1.185 g, 0.005 mol) in 30 cm^3 of DMF were placed in two-necked flask fitted with a condenser and capillary for argon supply, heated to 140°C under argon, kept at this temperature for 7 hours, cooled to room temperature and poured out in 100 ml of mixture acetone : water = 2 : 1, v. The beads were filtered off, washed with methanol, dried at 70°C for 10 h then in vacuum for 12 h. The mass of beads was 1.98 g.

Found: C – 75,73; H – 5,67; N – 9,26
Calc. for $C_{31}H_{23}N_3O_2 \cdot H_2O$: C – 76,38; H – 5,13; N – 8.62
λ_{max} cm^{-1} 1650 (C=N) and 1714 (aldehyde group) are observed.
λ_{max} cm^{-1} 3200 – 3400 (NH_2 – group) is absent.

2. The solution of dialdehyde – fluorophore (0.47 g, 0.001 mol) in 15 cm^3 of *N*-methylpyrrolidone and solution of 6-aminophenalenone

(0.39 g, 0.022 mol) in 10 cm^3 of *N*-methylpyrrolidone were placed in two-necked flask fitted with a condenser and capillary for argon supply, heated to 150°C under argon, kept at this temperature for 4 hours, heated to 180°C, kept for 5h, cooled to room temperature and poured out in 100 cm^3 of mixture 0.1 M HCl : ethanol = 1:1, v. The beads were filtered off, washed with water, ethanol, extracted by ethanol for 12 h, dried at 70°C for 7 h then in vacuum for 12 h. The mass of beads was 0.15 g.

Found: C – 77.00; H – 4.45; N – 8.02; Cl – 4.46
Calc. for $C_{58}H_{38}N_5O_2Cl$ C – 79.21; H – 4.40; N – 8.11; Cl – 411
λ_{max} cm^{-1} 1650 (C=N) is observed

Bifluorophore on the Basis of 3-aminobenzantron and 2,8-diamine-3,7-dimethylacrydine Hydrochloride(6)

Bifluorophore on the basis of 3-aminobenzantron and 2,8-diamine-3,7-dimethylacrydine) hydrochloride(6) was producted by the same method as bifluorophore on the basis 2,8-diamine-3,7-dimethylacrydine) hydrochloride(6) and 6-aminophenalenone(4)

The mass of beads was 0.51 g.
Found: C – 72.23; H – 5.02; N – 7.30; Cl – 3.82
Calc. for $C_{65}H_{42}N_5O_2Cl \cdot 6H_2O$ C – 73.06; H – 5.06; N – 6.56; Cl – 3.3
λ_{max} cm^{-1} 1650 (C=N) is observed

The UR-spectra were recorded on UR-20 instrument.

The absorption spectra of solutions of all investigated compounds in *N*-methylpyrrolidone were recorded at room temperature on Specord M-40 instrument, spectra of fluorescence and excitation of fluorescence – on Jobin Yvon 3CS instrument, ensuring automatic correction of spectra. The quantum yields of fluorescence were determined by a relative method [12]. The solution of 7-amino-4-methylcoumarin with a quantum yield of fluorescence = 0,61 [13] was used as the standard. For determination of quantum yield fluorescence for donor and acceptor fragments in biflyorophores their spectra of absorption and fluorescence were resolved into separate bands by the method of Alentsev-Fok [14].

References

[1] Svinarev, N. V., Kopilova, T. N., Galeeva, A. I., Artjuchov, V. Ja. and Majer, G. V. (1990). *Optics and Spectroscopy*, **68**(2), 349.

[2] Bogdanov, V. L., Klochchov, V. N. and Korsacova, E. G. (1992). *Optics and Spectroscopy*, **72**(1), 115.

[3] Schield, H. G. and Tirrel, D. A. (1992). *Macromolecules*, **25**(18), 4553.

[4] Sacharchuk, S. A. and Gorbatsevich, S. K. (1994). *J. of Applied Spectroscopy*, **60**(5-6), 416.

[5] Denisov, L. K. and Uginov, B. M. (1980). Chemistry of Heterocyclic Compounds, **12**(6), 723.

[6] Ischenko, A. A. *The Structure and Luminescent Property of Polymethyne Dyes.*

[7] Siling, S. A. Lozinskaja, E. I. and Borisevich, Ju. E. (1997). *Oxidation Comm.*, **20**, 149.

[8] Lindeman, S. V., Andrianov, V. G. *et al.* (1981). *J. of the Structural Chemistry*, **22**(4), 123.

[9] Dewar, M. J. S., Zoebisch, E. F., Healy, E. F. and Stewart, J. J. (1985). *J. Am. Chem. Soc.*, **107**, 3903.

[10] Ermolaev, V. L., Bodunov, E. N., Sveshnikova, E. B. *et al.* (1977). Non-radiation transfer of energy of electronic excitation, L., p. 310.

[11] Majer, G. V., Kopilova, T. N. *et al.* (1993). *Optics and Spectroscopy*, **75**(2), 337.

[12] Parker, C. (1972). Photoluminescence of solutions. Moscow, p. 247.

[13] Levshin, L. V. and Saletski, L. V. (1994). Optical methods of research of molecular systems, MSU, Moscow, p. 320.

[14] Fok, M. V. (1972). *Investigations of FIAS*, **59**, 3.