New reactions, functional compounds, and materials in the series of coumarin and its analogs*

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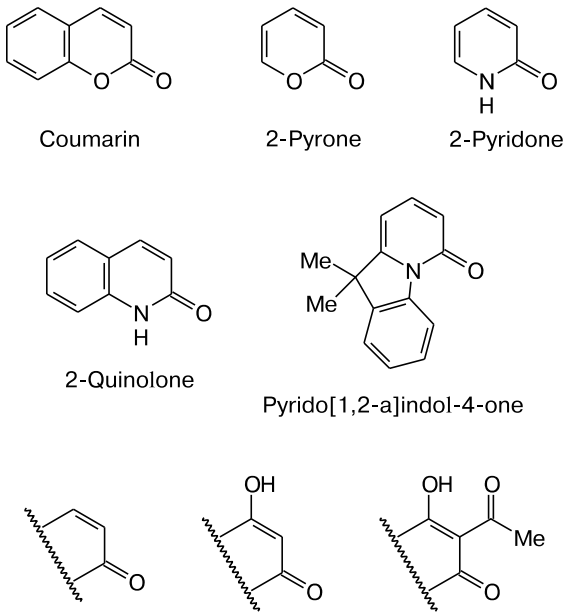
Data on the development of new functional compounds and materials based on the study of the reactions of coumarin and its analogs are generalized. Since coumarin derivatives are characterized by enhanced photochemically activity, special attention is given to the synthesis of photosensitive compounds and materials with intense fluorescence, including the structures capable of changing fluorescence under the action of various factors: solvent, pH of the medium, and interaction with bioorganic substrates. Pathways for design of fluorescent polymethine dyes, fluorescent labels for proteins, fluorescent photochromes, and photoacids for optical data storage with fluorescence read-out are reviewed. The role of isomerization transformations of the new compounds in their sensorial effects is established.

Key words: coumarins and their analogs, photochemical activity, fluorescence, polymethine dyes, photochromes, photoacids, optical data storage, sensors.

Derivatives of coumarin and its analogs, in particular, 2-pyrone, 2-pyridone, 2-quinolone, and pyrido[1,2-*a*]-indol-4-one, are characterized by pronounced photochemical activity, and some of them have intense fluorescence and are known as laser dyes.[1—5] In recent years researchers exhibited a significant increase in interest in coumarin derivatives and, first of all, in those capable of changing fluorescence under the influence of various factors: nature of the solvent, pH of the medium, irradiation, and interaction with bioorganic substrates.[6—10] These properties provide the possibility of using these compounds for the design of new functional materials suitable for optoelectronics, optical data recording and sensor elements and devices.[11—13]



1. Reactions of boron difluoride complexes of coumarin derivatives and its analogs. Synthesis of new polymethine dyes

The derivatives of coumarin and its analogs, particularly, 2-pyrone, 2-pyridone, 2-quinolone, and pyrido[1,2-*a*]-indol-4-one containing acyl and hydroxy groups in the lactone (or lactam) ring as shown below were used as the starting compounds in syntheses of new functional compounds and materials.

In the presence of hydroxy and carbonyl groups in the indicated positions, these hetarenes belong to β-di- and β,β-tricarbonyl compounds potentially suitable for synthetic purposes. These compounds are especially prone to tautomeric transformations, as it exemplified by 3-acetyl-4-hydroxycoumarin[14—16] (Scheme 1).

Undoubtedly, these transformations can be considered as a certain prerequisite for high reactivity of the corresponding acyl(hydroxy)hetarenes. At the same time, the

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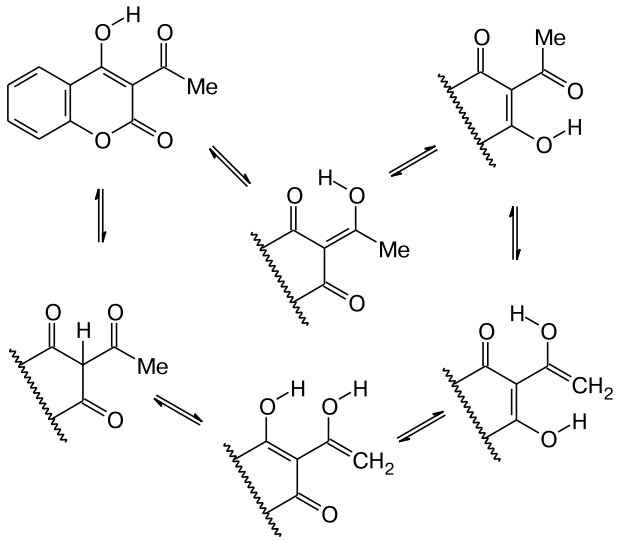
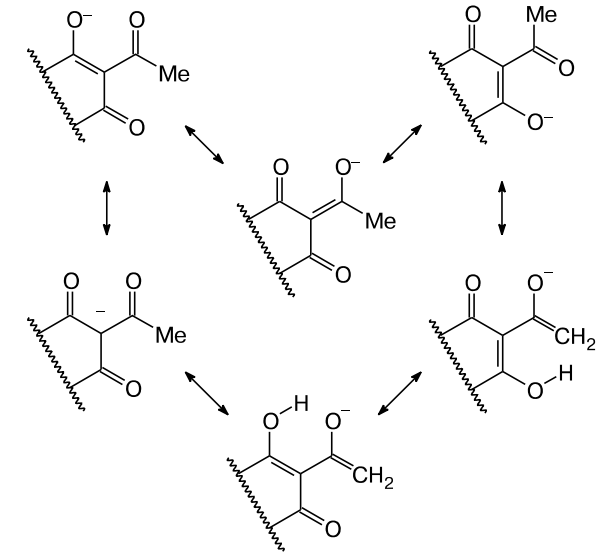
Scheme 1



shown tautomeric transitions objectively impede practical applications of β-di- and β,β-tricarbonyl compounds of hetarenes in synthesis. For example, the ionization of 3-acetyl-4-hydroxycoumarin leads to the formation of an anion, the negative charge in which is delocalized at least on four atoms in six resonance structures (Scheme 2).

Scheme 2



Naturally, the subsequent interaction of this anion, in particular, with electrophilic reagents should proceed rather ambiguously and can result in the formation of a complicated mixture of products.

We established that the listed above acyl(hydroxy)-hetarenes react with boron trifluoride etherate readily to form boron difluoride complexes characterized by high synthetic potential, valuable spectral properties, and pronounced biological activity.[17—21]

A specific structure of the boron difluoride complexes of the discussed acyl(hydroxy)hetarenes is the formation of a planar bipolar pseudo-aromatic cycle including the boron atom and two oxygen atoms. This fact is illustrated by the equalization of two C—O, two C—C, and two B—O bonds, respectively, in the boron difluoride complex of 3-acetyl-4-hydroxycoumarin (**1**)[17,18] (Fig. 1).

Analogous boron difluoride complexes of other hetarenes were studied by X-ray diffraction analysis.[19,20] All complexes synthesized are rather hydrolytically stable, which also indicates the covalent character of the B—O bonds.

A substantial rearrangement of the electronic and geometric structure of the ligand molecule is accompanied by a significant change in its reactivity, including that in aldol condensation reactions.[19—23] For example, the reactions of boron complexes of acyl(hydroxy)coumarins **1—3** with ethyl orthoformate smoothly afforded symmetric polymethine dyes **4—6** (Scheme 3).

The intense narrow band at 567—596 nm with the vibrational structure characteristic of the polymethine dyes is observed in the electronic absorption spectra of dyes **4—6** (Fig. 2). As all polymethine dyes, compounds **4—6** have high molar absorption coefficients (ε = 96 000—145 000).

Compound **4** in a chloroform solution has noticeable fluorescence at λ_{max} = 595 nm. The emission spectrum retains the same vibrational structure as in the absorption spectrum. Since the polyene system of compound **4** bears

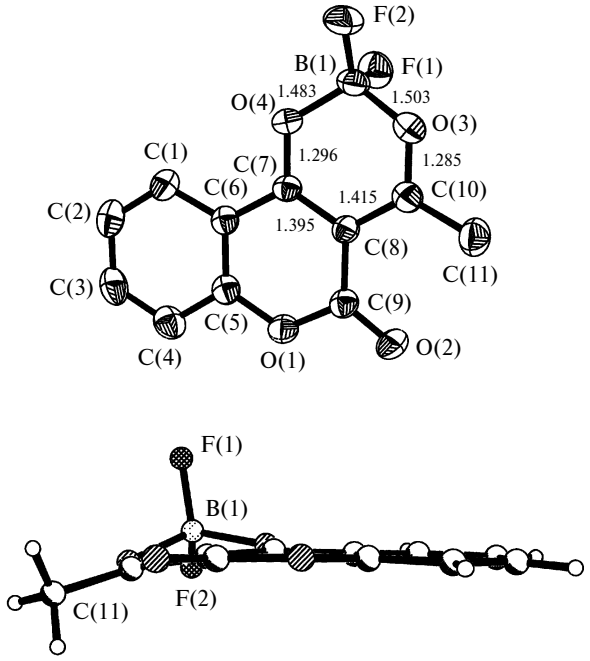
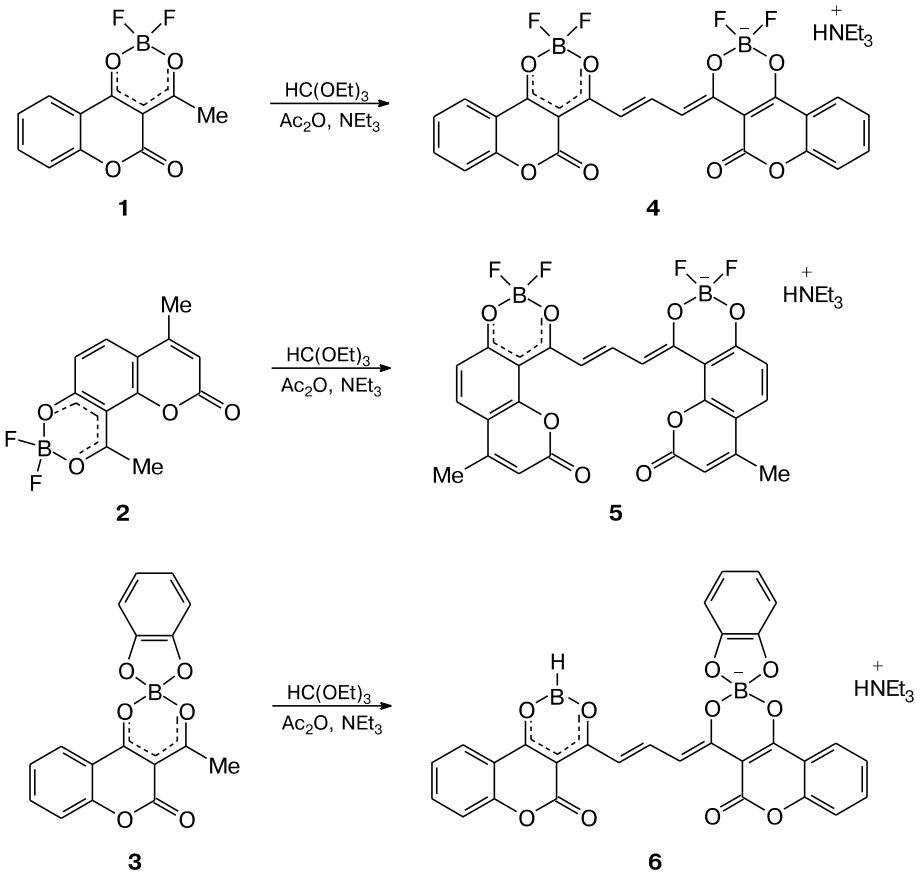


Fig. 1. Molecule of complex **1** (X-ray diffraction data). Bond lengths are given in Å. Two projections are shown.

Scheme 3



the negative charge (unlike the most part of the polymethine dyes bearing, as a rule, a positive charge), this compound turned out to be suitable for dyeing tissues containing amide groups (wool, silk, polycaprolactam). The dyeings obtained are smooth and fluorescent.

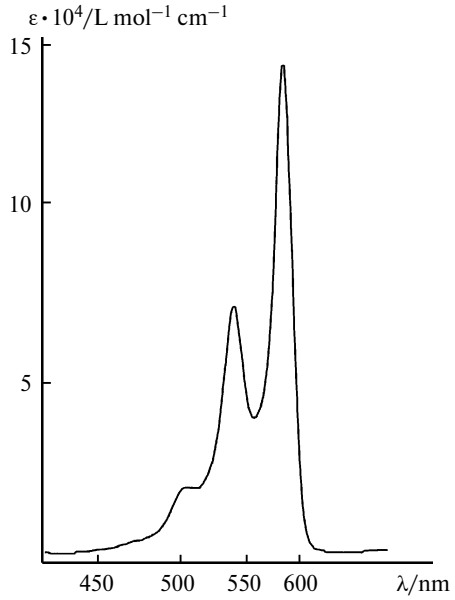


Fig. 2. Electronic absorption spectrum of compound **4** in $CHCl_3$.

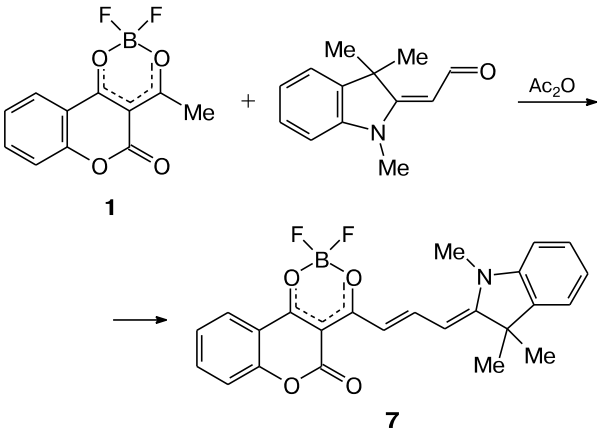
Boron difluoride complex **1** also smoothly forms nonsymmetric polymethine dyes. For example, the reaction of compound **1** with 1,3,3-trimethyl-2-formylmethylidene indolenine (Fischer´s aldehyde) in acetic anhydride gave dye **7** as large blue crystals with metallic luster. Dye **7** has an absorption maximum at 569 nm, and its molar absorption coefficient is ε = 98 200 (Scheme 4).

When boron difluoride complex **8** was used for condensation with Fischer´s aldehyde in acetic anhydride, compound **9** with the absorption maximum at 431 nm and molar absorption coefficient ε = 62 000 is formed (Scheme 5).

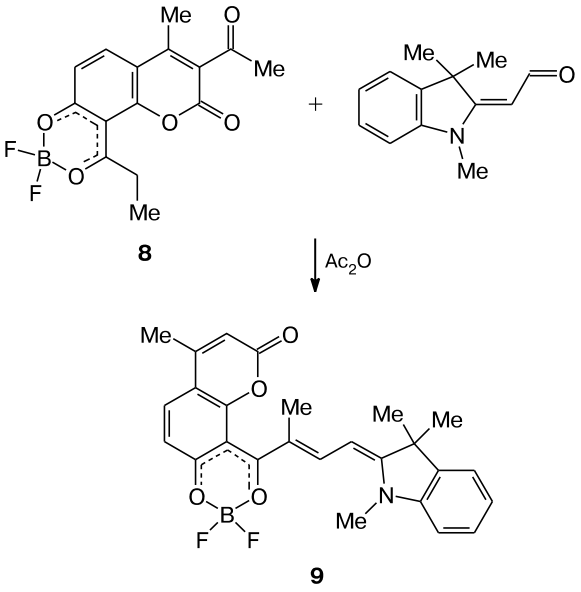
Another method for synthesis of nonsymmetric polymethine dyes is the reactions of boron difluoride complex **10** with the compounds containing active methyl groups. Complex **10**, which can be considered as a hemicyanine dye, was obtained by the reaction of compound **1** with DMF in acetic anhydride (Scheme 6).

Enamine **10** readily undergoes condensation reactions with the compounds containing methyl groups with enhanced CH acidity. So, the reaction of compound **10** with 1,2-dimethylquinolinium iodide in acetic anhydride in the

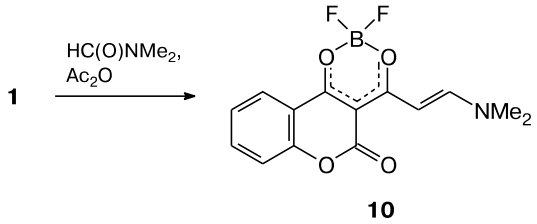
Scheme 4



Scheme 5



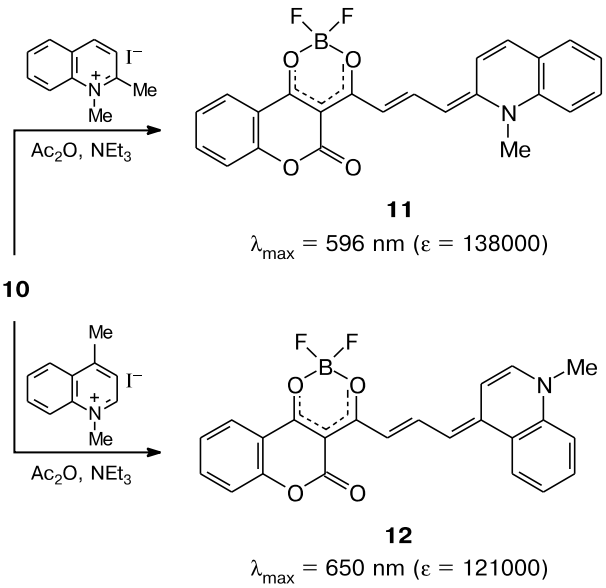
Scheme 6



presence of triethylamine at 90 °C for 30 min afforded unsymmetric polymethine dye **11** (Scheme 7).

The electronic absorption spectrum of compound **11** exhibits the narrow intense absorption band with a maximum at 596 nm and a molar absorption coefficient of

Scheme 7



138 000. As in the case of other polymethine dyes, the long-wavelength absorption band has a pronounced vibrational structure.

Under similar conditions, the reaction of compound **10** with 1,4-dimethylquinolinium iodide afforded compound **12**, whose electronic spectrum exhibits one narrow intense band at 650 nm (ε = 121 000) with the pronounced vibrational structure.

The application of the new boron difluoride complexes made it possible to produce the cinnamoyl derivatives of the above listed hetarenes in the preparative scale (Scheme 8).[19–23]

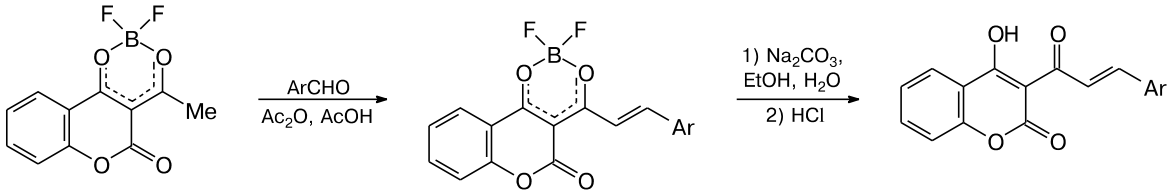
Both the cinnamoyl derivatives and their boron difluoride complexes have unique spectral properties. The spectral properties of the cinnamoyl derivative of dehydroacetic acid and pyrido[1,2-*a*]indol-4-one are shown as an example in Table 1 (Scheme 9).

Table 1. Spectral properties of cinnamoyl derivatives of dehydroacetic acid **15**, pyrido[1,2-*a*]indole **18**, and their boron difluoride complexes **14** and **17**

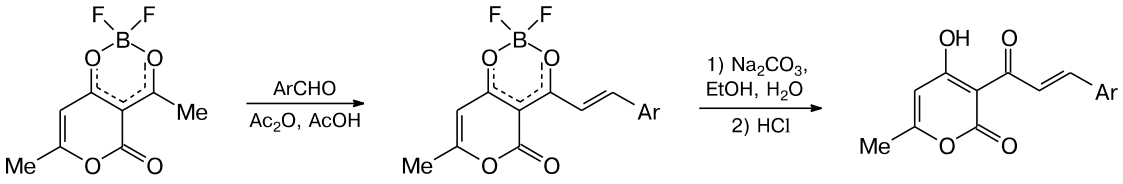
Compound	λ^{fl}_{ex}	λ^{fl}_{em}	Stokes shift	$\lambda^{abs}_{max}/(\varepsilon)$
	/nm			
14a	634	701	67	620 (100000)[a]
15a	534	553	19	530 (35000)[a]
14m				554 (192483)[b]
15h	505	566	61	492 (24240)[b]
17a	588	609	21	560 (120000)[a]
18a	478	516	38	458 (45296)[b]

Note. The fluorescence spectra were recorded in CCl_4.
[a] In CCl_4.
[b] In $CHCl_3$.

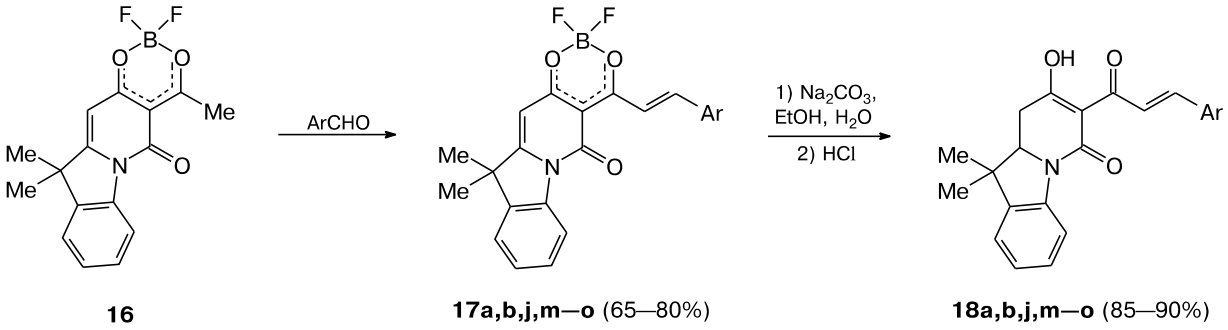
Scheme 8



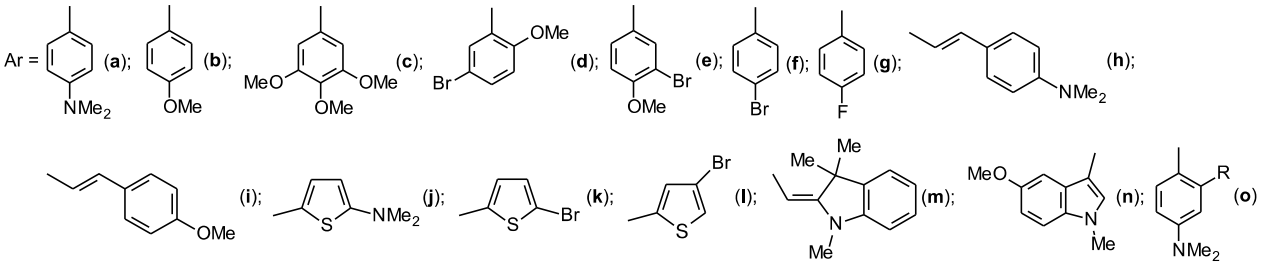
Scheme 9



13 **14a—m** (65—80%) **15a—m** (75—90%)



16 **17a,b,j,m—o** (65—80%) **18a,b,j,m—o** (85—90%)



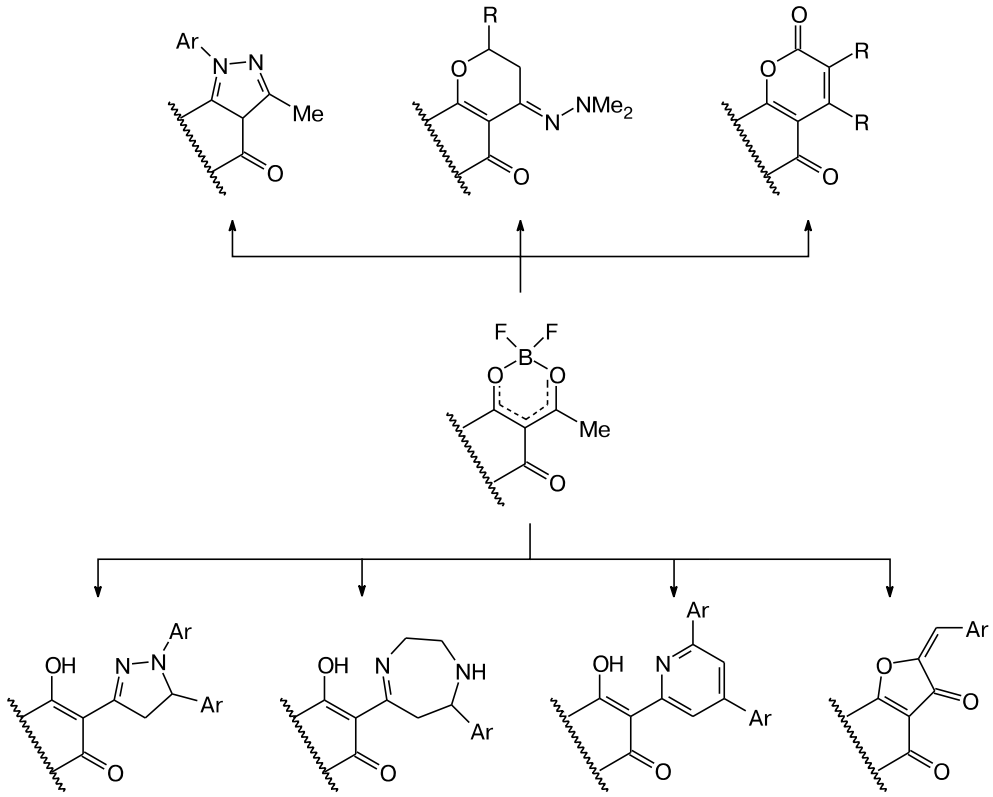
R = OAc (**17o**), OH (**18o**)

The electronic absorption spectra of the cinnamoyl derivative in the visible spectral range have an intense absorption band. The strong hypsochromic shift (up to 100 nm) is observed in the absorption spectra on going from the boron difluoride complexes to their hydrolysis products. Both the boron difluoride complexes of the cinnamoyl derivatives and free bases are characterized by intense fluororescence.

In turn, the cinnamoyl derivatives turned out to be convenient starting compounds in synthesis of many hetarene and hetaryl derivatives, namely, pyrazolohetarenes, α- and γ-pyronohetarenes, and pyrazolinyl-, pyridyl-, and diazepinylhetarenes (Scheme 10).[24—26]

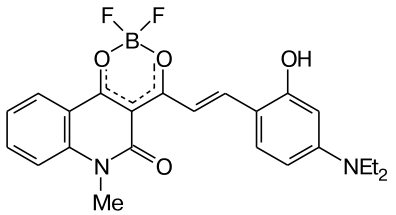
New hetarene and hetaryl derivatives have valuable spectral properties, and some of them are also characterized by photochemical activity (see section 4).

Scheme 10



2. Fluorescent labels for proteins

Organic compounds are widely used in biochemical and medical investigations as optical labels for biomolecules.[26,27] It has recently been found that the polymethine dyes can also serve as efficient substrates for noncovalent fluorescence recognition of proteins.[28,29] Among the fluorescent labels for proteins, the coumarin derivatives are also known.[30] We found by electronic absorption and emission spectroscopy that the fluorescence of some new cinnamoylhetarenes and their boron difluoride complexes increases sharply on contact with proteins.[31] The changes in the emission spectra of the complex of cinnamoyl derivative of 4-hydroxy-2-quinolone **19** in the presence of bovine serum albumin (BSA) (curve *2*) and BSA and sodium dodecyl sulfate (curve *3*) compared to its spectrum in a buffer solution (curve *1*, 50-fold amplification) are shown in Fig. 3.



19

It is known that the ability of organic compounds to act as protein markers is caused by their capability of intercalating with bioorganic substrates. There are serious grounds to assume that the boron difluoride complexes of cinnamoylhetarenes interact with protein much more efficiently than the free ligands, *i.e.*, cinnamoylhetarenes. For example, in the presence of BSA the increase in the fluorescence of the boron difluoride complexes of 4-hy-

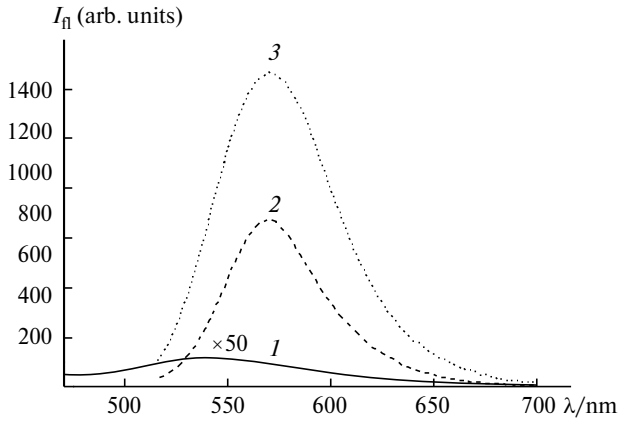
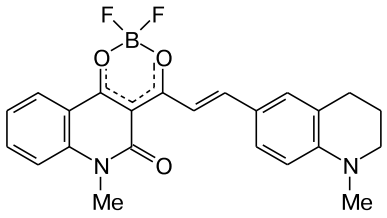


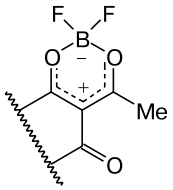
Fig. 3. Fluorescence emission spectra of compound **19** in a Tris-HCl buffer (pH 8.0) in the absence (*1*) and in the presence of BSA (*2*) and BSA and sodium dodecyl sulfate (*3*).

droxy-3-cinnamoyl-2-quinolones **19** and **20** is 500 and 900 times, respectively, and that for the corresponding free ligands is only 100 and 200 times, respectively.



20

As follows from the X-ray diffraction results presented for the boron difluoride complexes of 3-acyl-4-hydroxyhetarenes, the 1,3,2-dioxaborane fragment formed by the reaction of the corresponding hetarene with boron trifluoride etherate is planar. At the same time, being the product of the donor—acceptor interaction of 3-acyl-4-hydroxyhetarene with boron trifluoride, this fragment should inevitably be dipole, which is shown below.



It is reasonable to assume that the planar bipolar structure of this fragment characterized by a pronounced ability to form intra- and intermolecular hydrogen bonds favors the intercalation of the boron difluoride complex of hetarene into the protein structure.[32,33]

As a rule, noncovalent binding accompanying the formation of a protein—dye complex is characterized by the shift of the absorption band maximum of the fluorophore in the electronic spectrum along with the fluorescence increase. The bathochromic shift of the absorption and fluorescence band maxima is also observed for the compounds studied in the presence of protein. For compound **19** these shifts are 69 and 79 nm. This fact in addition to the high increase in the fluorescence intensity and shift of the absorption and emission maxima to the IR range make promising the further search for fluorescent sensors in the discussed series of the coumarin derivatives, as well as a deeper analysis of the interaction of compound **19** with BSA.

3. Fluorescent photochromes

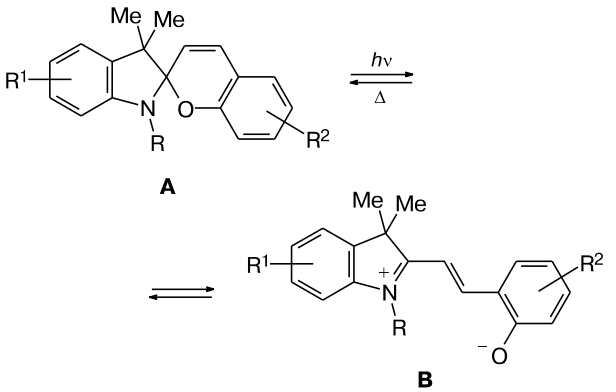
Onrush of computer and information technologies forms demand in more highly productive data recording systems capable of retaining, reproducing, and processing of huge data volumes.[34—40] One of the most promising directions of increasing the volume of recorded information on optical carriers is its volume recording using two-photon absorption for data storage and processing. When using fluorescence read-out, this method makes it possible to obtain basically new possibilities of information registration compared to the modern optical media of the DVD or Blue-Ray type based on data recording on the polymer disc surface.

Two technologies of data recording and reproducing on optical discs are used: (1) optical WERM discs (Write Erase Read Many times) are used for multiple recording—read-out cycles and (2) optical WORM discs (Write Once Read Many times) are used for single data recording and multiple read-out. The WERM technology is based on the use of detection media that reversibly change the spectral properties upon irradiation. The main components of these media are organic photochromic compounds. Our results on the preparation of photochromes appropriate for reversible data recording are generalized in this section. A specific feature of new photochromes is not only the change in the color after irradiation but also the corresponding changes in fluorescence.

3.1. Fluorescent spiropyrans

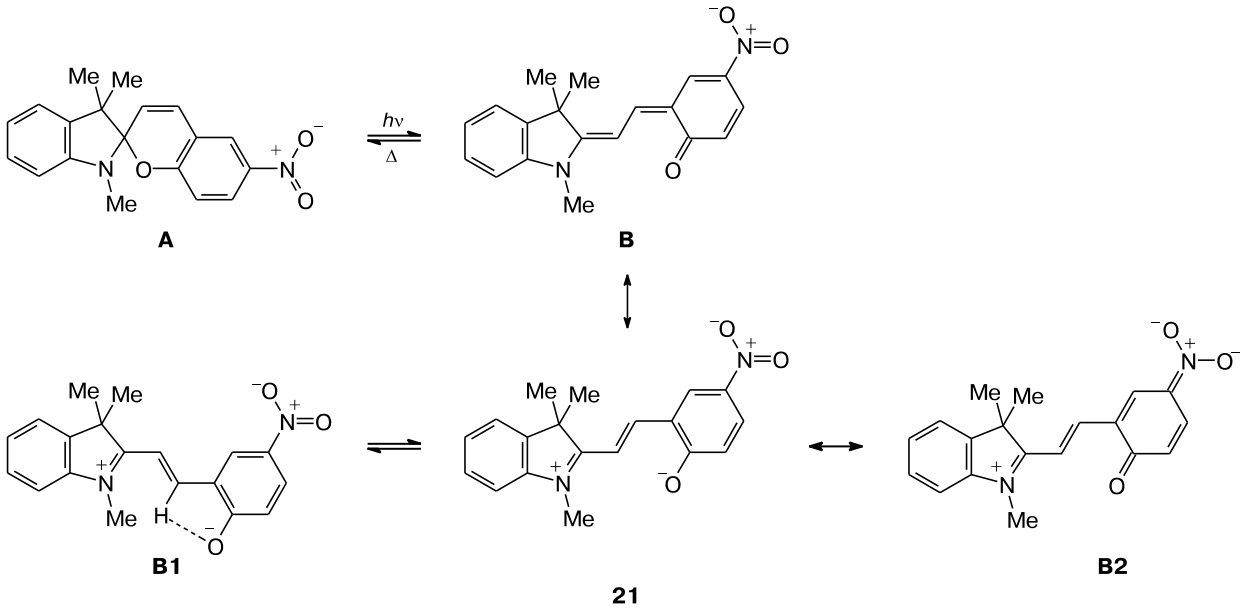
Indoline spiropyrans and their heteroanalogs are among the most intensively studied photochromic compounds.[38—40] This is due to prospects of their use in various areas of molecular electronics: optical systems of data recording and storage, dynamic chemi- and biosensors, systems of solar energy accumulation, molecular switches, and others. The photochromic properties of indoline spiropyrans are based on the photoinduced reaction of pyran ring opening accompanied by the thermal *cis—trans*-isomerization of the open form with the formation of colored merocyanine followed by the thermal or photochemical recyclization of the open form to the initial colorless spiro compound. The mutual transformations of the spiro (**A**) and open (**B**) merocyanine forms are shown in Scheme 11 using spiro-2*H*-1-benzopyran-2,2′-indoline as an example.

Scheme 11



R = H (**a**), Me (**b**), Br (**c**), NO_2 (**d**), MeO (**e**)

Scheme 12

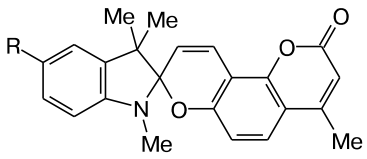


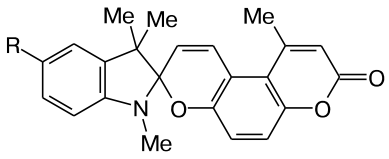
The absorption wavelength of the open form, the lifetime of this form, and the quantum yield of the reaction are important parameters of the photochromic processes. The change in the structure of the spiro derivative exerts a significant effect on these parameters. The role of one of the structural factors, *viz.*, the nature of the substituent in the benzopyran fragment of spiro[2*H*-1-benzopyran-2,2′-indoline] **21**, is shown in Scheme 12. The introduction of the strong electron acceptor (nitro groups) into the benzopyran fragment leads to the resonance delocalization of the negative charge induced on this fragment upon pyran ring opening and, as a consequence, to an increase in the lifetime of the open (merocyanine) form of spiropyran. It is most likely that structure **B1** containing the hydrogen bond and quinoid structure **B2** contribute mostly to the stabilization of the merocyanine structure.

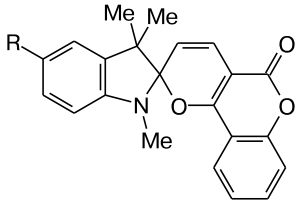
There are numerous published data on the influence of both substituents in the fused benzene rings and different heteroatoms in the indoline and benzopyran fragments on photochromism. In particular, the spiro compounds containing in benzoxazine, phenanthrolinoxazine, or naphthoxazine moieties instead of the benzopyran fragment were synthesized and studied.[38,39]

Spiropyrans changing both the absorption and emission spectra on going from the cyclic to merocyanine form are of special interest. From this point of view, coumarin derivatives can be very promising, which was confirmed by the synthesis and study of spiropyrans **22**—**24** containing the coumarin moieties.[41—43]

These spiropyrans were synthesized according to the Wizinger—Wennig method[44] by the condensation of Fischer´s base (or its heterocyclic analog) and hydroxyformylcoumarin. The ^{1}H NMR spectra unambiguously


22a—e


23a—c

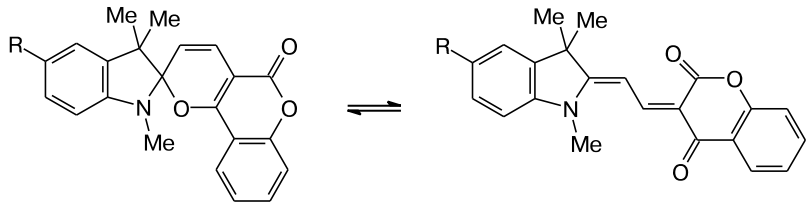

24a—d

R = H (**a**), Me (**b**), Br (**c**), NO_2 (**d**), MeO (**e**)

indicate that before irradiation spiropyrans **22** and **23** exist in solution in the cyclic form and spiropyrans **24** exist in the open (merocyanine) form (Scheme 13).

An analysis of the ^{1}H NMR spectra of compounds **24** unexpectedly revealed the appearance of two doublets attributed to the methine protons, which was explained using the quantum chemical calculations by the possibility of existence of the merocyanine form in two configurations, *viz.*, *cis* and *trans*, with respect to the C(2)—C(4) double bond (Scheme 14).[41]

Scheme 13

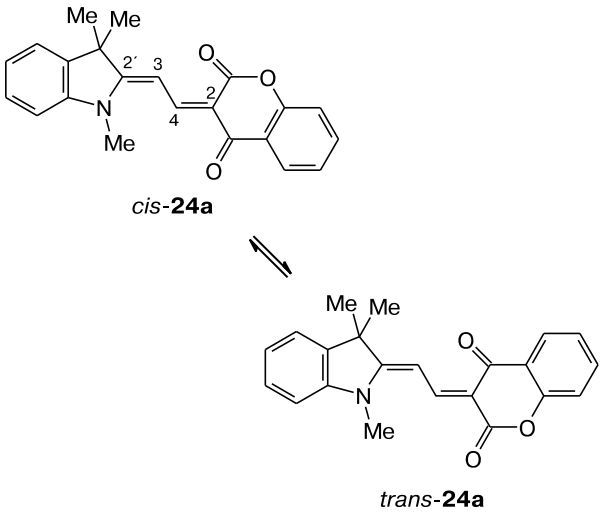


24

Compounds **22**—**24** possess pronounced fluorescence (Figs 4 and 5).

A comparative study of the photochromic properties of the synthesized indoline spiropyrans with different structures of the coumarin moiety revealed that compounds **22** based on 8-formyl-7-hydroxy-4-methylcoumarin[42,43] have the most pronounced photochromic properties (Fig. 6).

Scheme 14



cis-**24a**

trans-**24a**

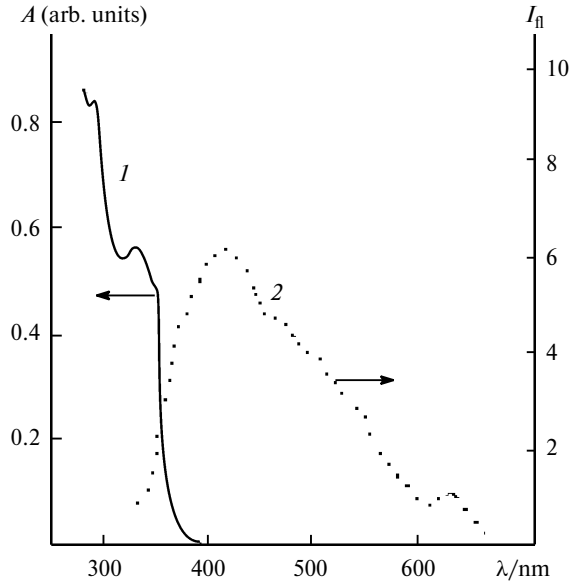


Fig. 4. Absorption (*1*) and fluorescence (*2*) spectra of compound **22a** in toluene ($C = 0.5 \cdot 10^{-4}$ mol L^{-1}).

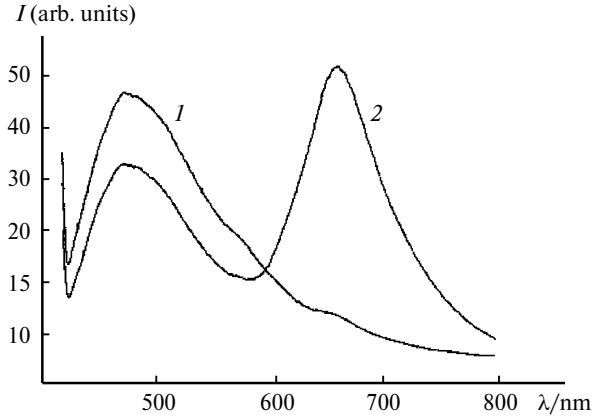


Fig. 5. Fluorescence spectra of spiropyran **22b** in benzene ($C = 1 \cdot 10^{-3}$ mol L^{-1}) before (*1*) and after (*2*) UV irradiation.

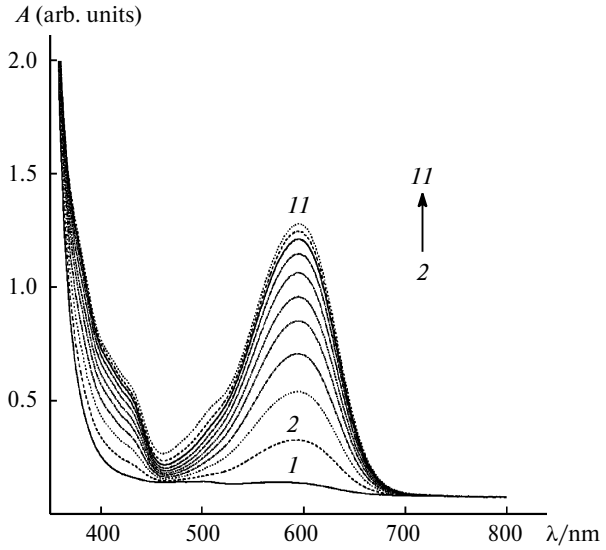
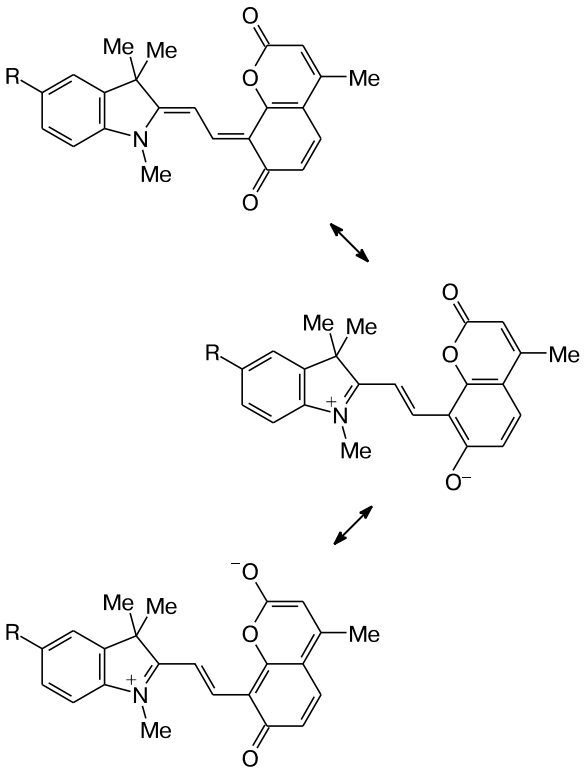


Fig. 6. Absorption spectra of the initial (*1*) and photoinduced forms of **22c** at continuous UV irradiation (*2*—*11*) in poly(methyl methacrylate).

Spiropyrans **23** synthesized using 8-formyl-6-hydroxy-4-methylcoumarin are characterized by the short lifetime of the photoinduced merocyanine form at ambient temperature. Under usual conditions, compounds **24** based on 3-formyl-4-hydroxycoumarin turned out to be nonphotochromic and exist only in the merocyanine form. According to the quantum chemical calculations, the obtained experimental data are explained by differences in the negative charge delocalization on different coumarin moieties in the open forms of spiropyrans. As can be seen from the resonance structure of merocyanines **22**—**24** (Schemes 15—17, only the most stable resonance structure according to the AM1 calculations are shown), the conditions for the negative charge delocalization differ in the 7-hydroxy-, 6-hydroxy-, and 4-hydroxycoumarin fragments. Each open form of compounds **22** and **24** has three resonance structures (see Schemes 15 and 16).

Scheme 15

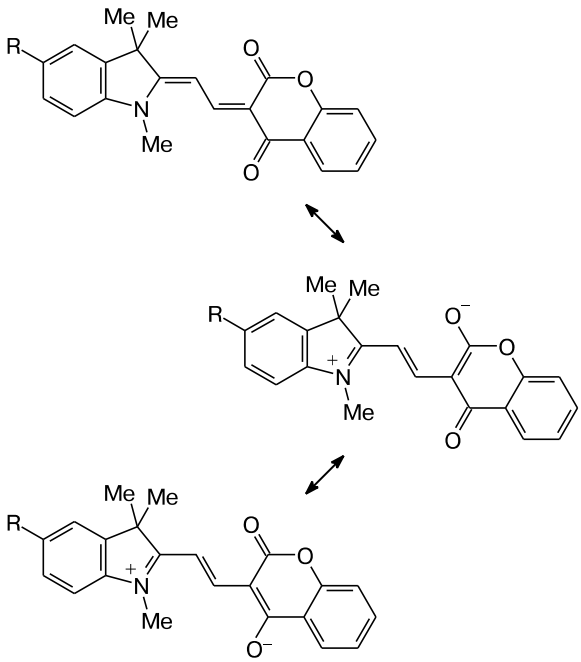


22

Compounds **23** have only two stable resonance structures (see Scheme 17).

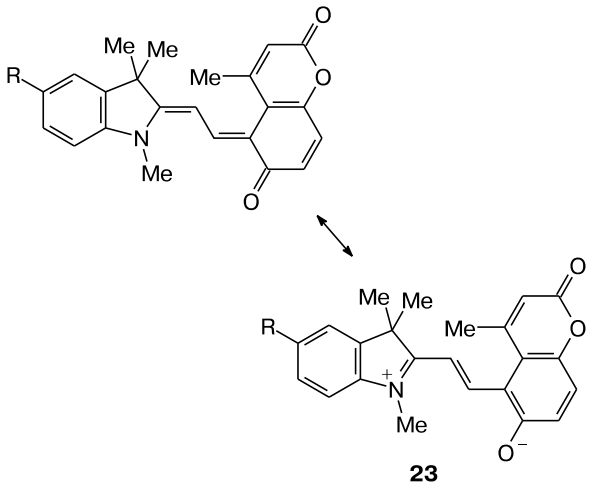
It follows from the calculated heats of formation ΔH° for the cyclic and open forms of spiro compounds **22**—**24** that the 1,3-diketo form of compounds **24** is characterized by especially high stability. It is most likely that due to this these compounds exist exclusively in the open form in the studied temperature range.

Scheme 16



24

Scheme 17



23

Spiropyrans **22** have a less stable open form. Therefore, the heats of formation of the spiro and open forms of these compounds are closest, which is a reason for the pronounced ability of compounds **22** to reversible phototransformations.

The open forms of spiropyrans **23** are least stable, and their heats of formation are considerably higher than that of the cyclic forms of these compounds. It is most likely that this circumstance is the main reason for especially high rates of thermal decoloration of spiro compounds **23**.

The study of photochromism of indoline spiropyrans of the coumarin series **22**—**24** in polymer blocks and films showed that these photochromic compounds, which in solutions experience fast relaxation from the photoinduced merocyanine form to the initial spiro form, in poly(methyl methacrylate) sharply decrease the relaxation rate to a value appropriate for practical application of the corresponding polymer photochromic materials.[43] As in solutions, in polymer matrices the photochromic compounds exhibit photoinduced fluorescence caused by the formation of the photoinduced merocyanine form.

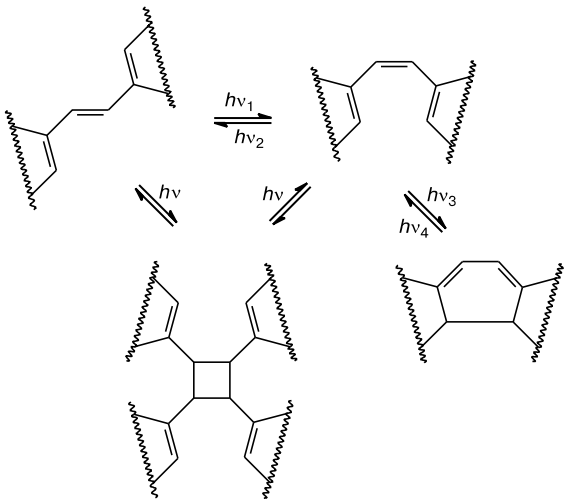
3.2. Photochromism of thienylcoumarinylthienyl-maleic anhydride

Another group of fluorescent photochromes (studied by us in detail) consists of coumarinyl(thienyl)ethene derivatives. Diaryl(hetaryl)ethenes differed by the structure of the ethene bridge and nature of the hetarene fragment are typically considered as very promising photochromes for using in systems of data recording and storage, which is explained by the efficiency of photoisomerization, thermal stability of both isomeric forms, and high cyclicity of phototransformations.[34—37] In the general case, diaryl(hetaryl)ethenes can undergo the following phototransformations (Scheme 18): (1) *E*—*Z*-isomerization, (2) cyclization of *Z*-isomer to form cyclohexadiene derivative, and (3) [2+2] cycloaddition with cyclobutane formation.

It should be mentioned that the most valuable structures contain the double (ethene) bond in the cycle, which prevents *cis*—*trans*-isomerization of the open form and thus provides the high yield of photoinduced cyclization. As in the case of spiropyrans, the structural modification of the diaryl(hetaryl)ethene system performed by us provided the inclusion of the coumarin moiety as a potential fluorophore into the chromophoric system of the photochrome. In particular, we synthesized a new photochrome: theinyl-(coumarinylthienyl)maleic anhydride **25** (Scheme 19).[45]

The key stage in the synthesis of photochrome **25** is the Suzuki—Miyaura cross-coupling of 3-bromocoumarin **26**

Scheme 18



and (5-methyl-2-thienyl)boronate **27** giving compound **28**. The optimization of the conditions (Table 2) allowed us to carry out this reaction in 84% yield. Compound **25** was obtained by the reaction of acid chloride **29** with thiopheneglyoxylic acid **30**.

The introduction of the coumarin moiety into the well studied photochromic system of 3,4-dithienylfuran-2,5-dione provided both the intense fluorescence of the open form and thermal stability of the cyclic form (Scheme 20, Figs 7 and 8).[45]

3.3. Photochromism of 4-(3-coumarinyl)-5-(thienyl)thiazoles

4-(3-Coumarinyl)-5-(thienyl)thiazoles **31** (R^1 = Me, R^2 = H) and **32** ($R^1 + R^2$ = CH=CHCH=CH) are attributed to a basically new group of photochromes, since both the photochromic and fluorescent fragments in their structures are involved in the single conjugation chain.[46,47]

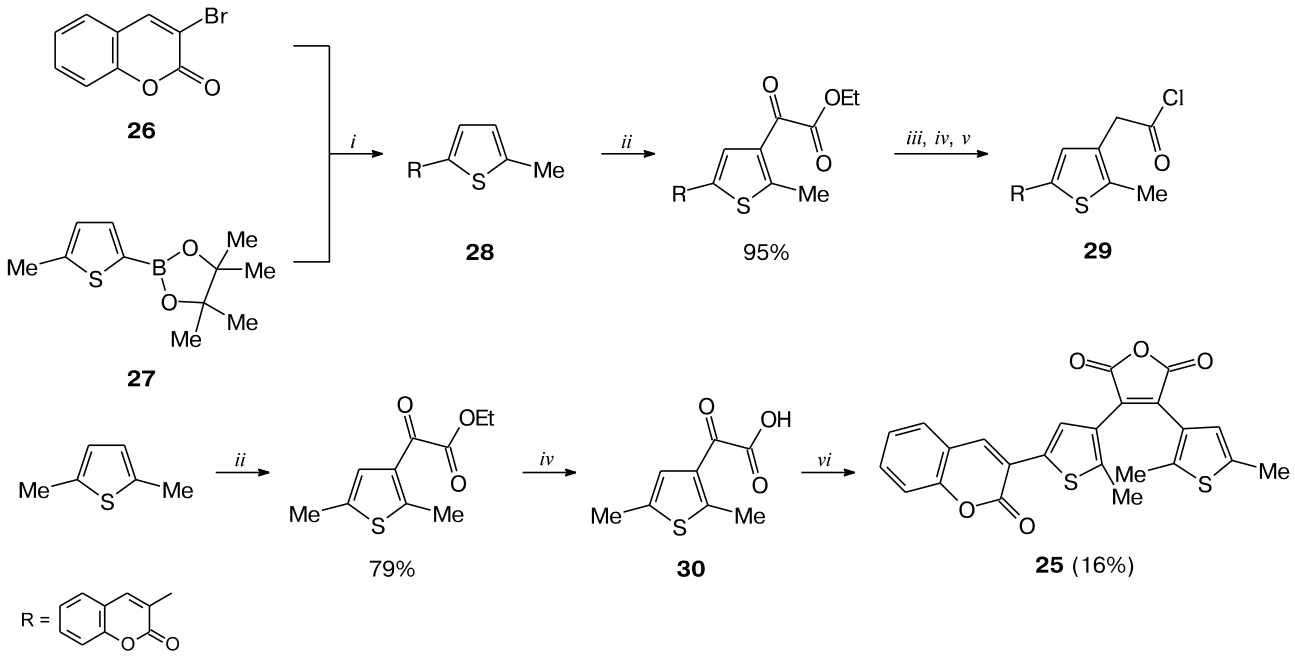
Photochromic 4-(3-coumarinyl)-5-(thienyl)thiazoles **31** and **32** were synthesized from 3-coumarinylacetic acid

Table 2. Optimization of the synthesis conditions for compound **28** by the cross-coupling reaction

Entry	Catalyst	Solvent	Base	Additive	*t*/h	Yield (%)
1	$Pd(PPh_3)_4$	Dioxane	CsF (3 equiv.)	—	10	34
2	$Pd(PPh_3)_4$	Dioxane	Na_2CO_3 (2.5 equiv.)	H_2O	6	—*
3	$Pd(PPh_3)_4$	MeCN	Na_2CO_3 (2.5 equiv.)	H_2O	6	36
4	$Pd(PPh_3)_4$	MeCN	CsF (5 equiv.)	—	48	21
5	$Pd(PPh_3)_4$	MeCN	K_3PO_4 (3 equiv.)	Bu_4NBr	9	15
6	$Pd(dppf)Cl_2$	MeCN	Na_2CO_3 (2.5 equiv.)	H_2O	36	55
7	$Pd(dppf)Cl_2$	MeCN	CsF (5 equiv.)	—	6	80
8	$Pd(dppf)Cl_2$	DMF	Na_2CO_3 (5 equiv.)	H_2O	3	75
9	$Pd(dppf)Cl_2$	DMF	CsF (5 equiv.)	—	3	84

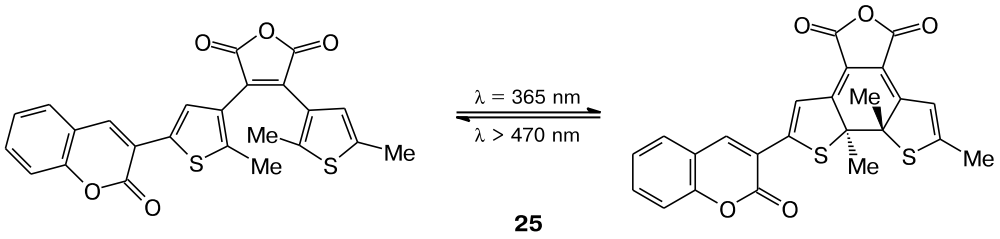
* Trace amounts.

Scheme 19



Reagents and yields: *i*. Pd (cat.); *ii*. EtOC(O)COCl, $AlCl_3$; *iii*. Et_3SiH, TFAA, 86%. *iv*. KOH, 74%; *v*. $SOCl_2$; *vi*. **29**, NEt_3.

Scheme 20



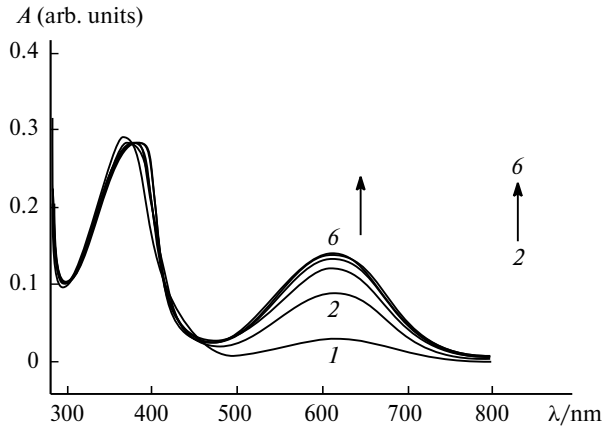


Fig. 7. Changes in the electronic absorption spectrum of compound **25** in a toluene solution before (*1*) and after (*2*—*6*) UV irradiation (365 nm) for 1 (*2*), 2 (*3*), 4 (*4*), 8 (*5*), and 16 s (*6*).

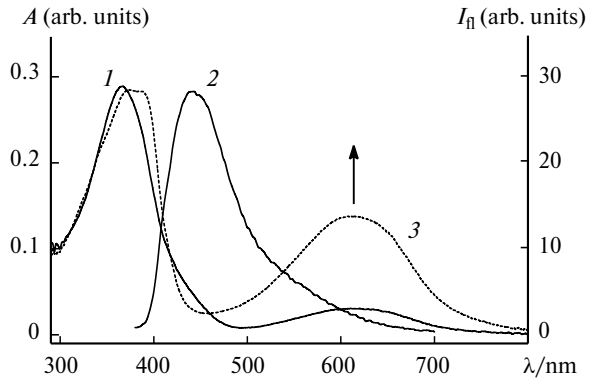


Fig. 8. Absorption (*1*) and fluorescence (*2*) spectra of the initial form and the absorption spectrum of the cyclic form (*3*) of compound **25**.

chloride. 1,2-Dihetarylethanones **33** were synthesized by the Friedel—Crafts reaction. They present wide possibilities of building bridged heterocyclic systems. The bromination of compounds **33a**,**b** yielded the corresponding bromoketones **34a**,**b**, which were reacted with thioamides of acetic, benzoic, and 4-methoxybenzoic acids, as well as with thiourea and phenylthiourea (Scheme 21).

4-(3-Coumarinyl)-5-(thienyl)thiazoles **31** and **32** synthesized undergo photocyclization (Scheme 22, Figs 9 and 10). UV irradiation of solutions of the open forms decreases the absorption intensity at 350—400 nm and increases the absorption intensity at 496—517 nm. The irradiation of the photoinduced cyclic forms of compounds **31** and **32** with light with the wavelength corresponding to their absorption maximum in the visible range results in backward phototransformations with the almost complete recovery of the absorption and fluorescence spectra of the initial form of the compound (see Scheme 22). On the whole, coumarinyl(thienyl)thiazoles have pronounced fluorescence of the open forms and high thermal stability

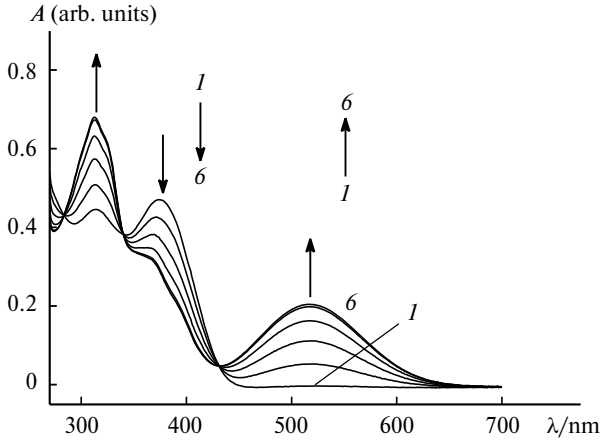
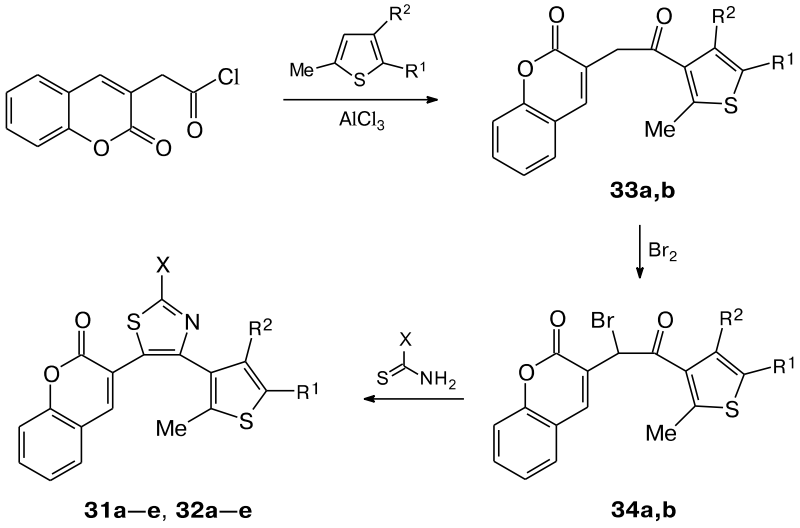


Fig. 9. Change in the absorption spectrum upon photocyclization of **31b**.

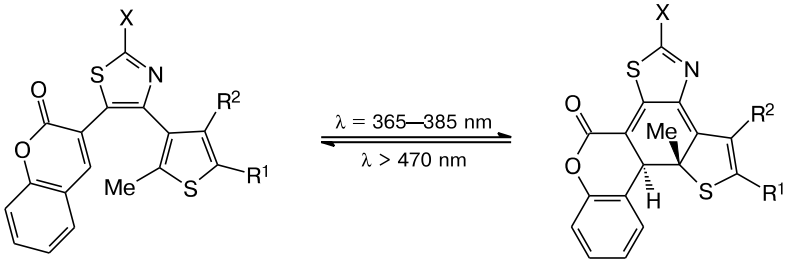
of the cyclic forms. It can be assumed that the introduction of the methyl group into position 4 of the coumarin

Scheme 21



31a—e, **33a**, **34a:** R^1 = Me, R^2 = H
32a—e, **33b**, **34b:** $R^1 + R^2$ = CH=CH—CH=CH
31, **32:** X = Me (**a**), Ph (**b**), 4-$OMeC_6H_4$ (**c**), NH_2 (**d**); NHPh (**e**)

Scheme 22



31, **32** (open form) **31**, **32** (cyclic form)

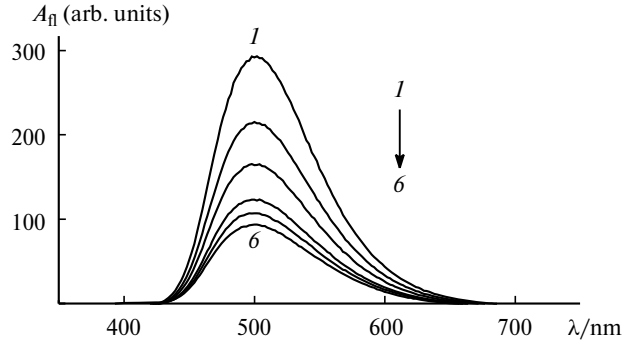


Fig. 10. Change in the fluorescence spectrum upon photocyclization of **31b**.

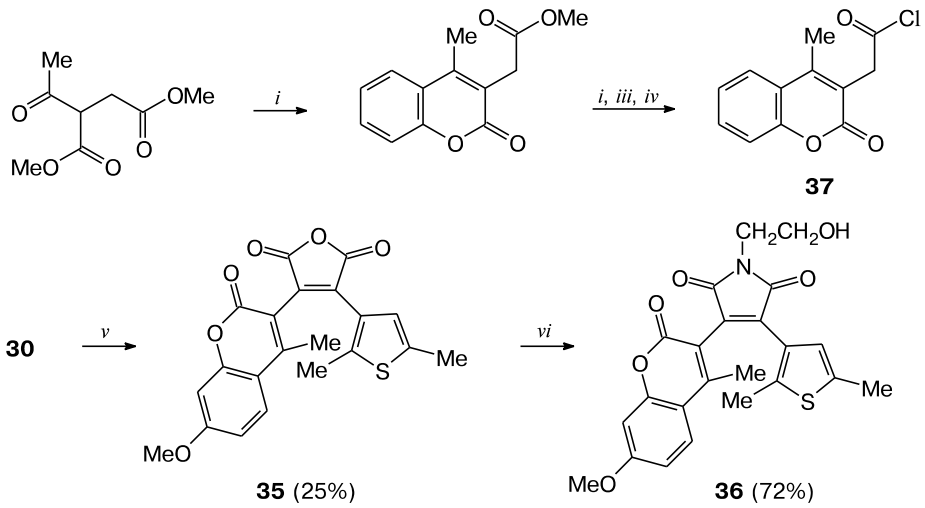
moiety will provide the further increase in stability of these new photochromic fluorophores.

3.4. Photochromism of coumarinyl(thienyl)maleic anhydride and maleimide

For the purpose of obtaining coumarinyl(hetaryl)ethenes with high photo- and thermal stability, we developed the scheme of the synthesis of cyclic derivatives of maleic acid including thiophene and coumarin fragments (Scheme 23).[48] Note that the fragments of maleic anhydride or maleimide are among the most promising heterocyclic "bridges" in dihetarylethene structures. As a rule, photochromic compounds bearing these fragments are characterized by thermal irreversibility of photocyclization and good photostability. In addition, the presence of the anhydride function provide wide possibilities for the modification of the structure of the photochromic compound and introduction of additional substituents (for example, fluorophores) or functional groups for copolymerization. The key stage of the synthesis of coumarinyl(thienyl)maleic anhydride **35** and maleimide **36** is the reaction of coumarinylacetic acid chloride **37** and thienylglyoxylic acid **30** (see Scheme 23).

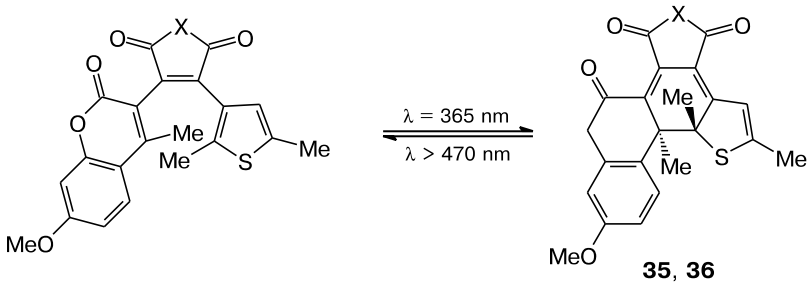
The cyclic (photoinduced) forms of compounds **35** and **36** undergo opening of the formed ring upon visible light irradiation (>450 nm) (Scheme 24). The photochromic transformations can multiply be performed without a substantial decrease in the absorbance at the absorption band of the photoinduced form (Figs 11 and 12).

Scheme 23



Reagents and yields: *i*. 1,3-$(HO)_2C_6H_3$, H_2SO_4, 43%; *ii*. Me_2SO_4, K_2CO_3, DMF, 74%; *iii*. KOH, 74%; *iv*. $SOCl_2$; *v*. **37**, NEt_3, CH_2Cl_2; *vi*. $HOCH_2CH_2NH_2$, MeOH.

Scheme 24



X = O, NCH_2CH_2OH

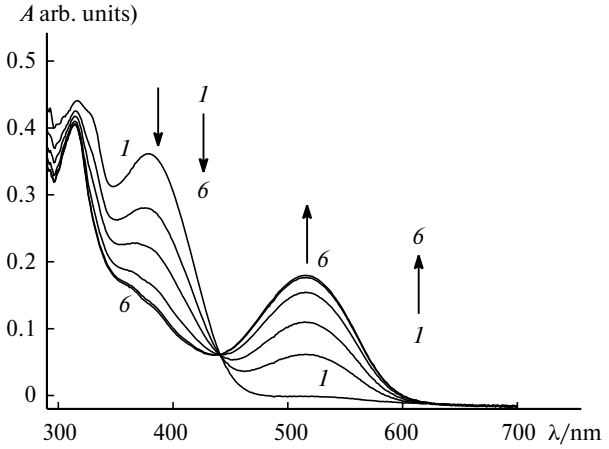


Fig. 11. Absorption spectra of maleimide **36** before (*1*) and after UV irradiation (365 nm) for 1 (*2*), 2 (*3*), 4 (*4*), 8 (*5*), and 16 (*6*) s.

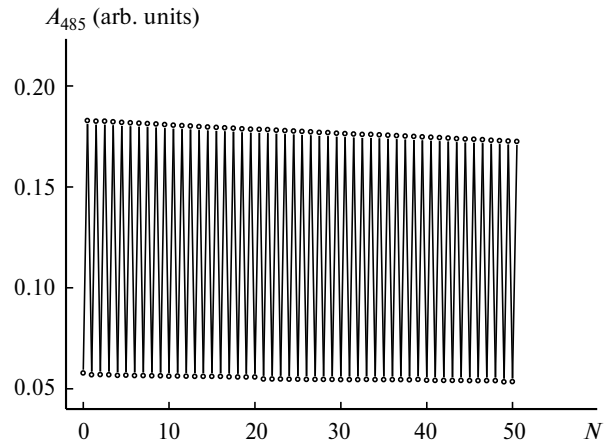


Fig. 12. Change in the absorbance at the absorption maximum of the cyclic form of compound **36** upon multiple irradiation with UV and visible light; *N* is number of photochromic cycle.

Photostability of maleimide **36** turned out higher than that of anhydride **35**: after 50 photochromic cycles the absorbance in the absorption band of the cyclic form is 94% of the initial value (in the first cycle) (see Fig. 12). A similar parameter for maleic anhydride **35** is 83%.

There are almost no published data on the direct comparison of fatigue resistance of photochromic dihetarylethenes with maleic anhydride and maleimide bridges (*i.e.*, for photochromes differed by the bridging fragment only). Nevertheless, it can be assumed that the difference found will be of general character when comparing the properties of similar structures.

4. New photoacids for optical data storage with fluorescence read-out

As already mentioned above, optical WORM discs are used for single data recording and multiple read-out, *viz.* optical data storage. Elements of data carried in WORM discs, so-called "pits," are formed due to the photochemical transformations of non-fluorescent precursors (initial substrates) into compounds with intense fluorescence (the backward process of fluorescence decay is also possible during the photochemical reaction). The following requirements are imposed on substances forming the pits: (1) the recorded, fluorescing form should have a high fluorescence quantum yield and (2) the precursor and photoproduct should have high thermal stability.[49,50]

For optical data storage, when a huge amount of information can be read-out only (without the possibility of cancellation), a fluorescent precursor is usually used.[50—54] Coumarins,[55] lactones and lactams of xanthene dyes of the rhodamine series,[50,56—58] thioindigo dyes, stilbene derivatives, substituted anthracene and anthraquinone, and other compounds[59,60] were studied as fluorescent precursors suitable for use in optical data recording systems.

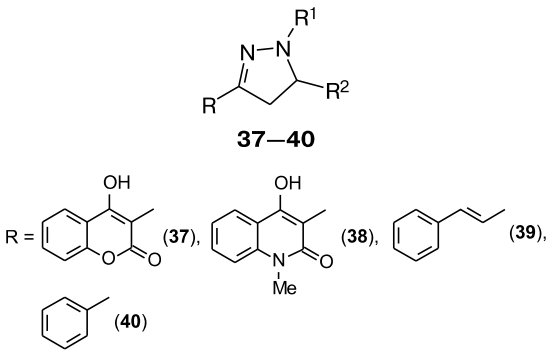
Fluorescence of some listed precursors, for instance, rhodamine dyes, can be activated only by means of irradiation, *i.e.*, in the absence of any additives. However, UV radiation needed for this purpose is rather drastic and results in the destruction of the dye. The irradiation of the precursor in the presence of a photoacid is less destructive if the fluorescence of this precursor is activated by the acid.

A photosensitive thermally stable compound, which after excitation with light with an appropriate wavelength undergoes photochemical transformation to form an acid, is used as a photoacid, or photoacid generator (PAG). This acid reacts with the fluorescent precursor to form a compound with intense fluorescence. Typical PAGs suitable for optical data storage are triarylsulfonium and triaryliodonium salts of some organic and inorganic acids, as well as nitronaphthaldehydes.[61—64]

Studying new photodetection media suitable for optical data storage, we found that some halogen-containing compounds can act as photoacids. However, the photoacidic properties of these compounds require the use of very drastic UV irradiation (UFS-1 lamp, λ_{max} = 254 nm), which remains the principal possibility of precursor photodestruction. Therefore, the search for photoacids capable of activating fluorescence of precursors by a longer-wavelength (less destructive) irradiation remains actual.

We have earlier reported the photodehydrogenation of 5-(*p*-anisyl)-3-(coumarin-3-yl)-1-phenylpyrazoline under irradiation in the presence of carbon tetrachloride.[65] It turned out that the photodehydrogenation of this pyrazoline is not the single example among the coumarin derivatives and analogs. In the study of the reaction discovered, we subjected pyrazolines **37—40** containing various substituents in positions 1, 3, and 5 to photodehydrogenation.[66] The data obtained are presented in Table 3. Since phototransformations of organics depend on the ability of the substances to absorb electromagnetic radiation, Table 3 presents the values of absorption band maxima and molar

absorption coefficients of compounds **37**—**40** in the electronic absorption spectra.



R^1 and R^2 are given in Table 3.

The majority of the studied compounds in a CCl_4 solution rapidly change the electronic absorption spectra under visible light irradiation. The transformation of the absorption spectrum of compound **37a** upon irradiation is shown as an example in Fig. 13, *a*. The spectral changes observed are not a consequence of the solvatochromic transformations of this compound, because the absorption spectrum of **37a** in a CCl_4 solution remains unchanged for a long time on keeping in the dark. These changes are not either caused by tautomeric transitions, which follows from the absorption spectra shown in Fig. 13, *b*.

To establish reasons for changing the electronic absorption spectrum of compound **37a** upon irradiation, we carried out a photo experiment at high concentrations monitoring the reaction course by the ^1H NMR spectra.

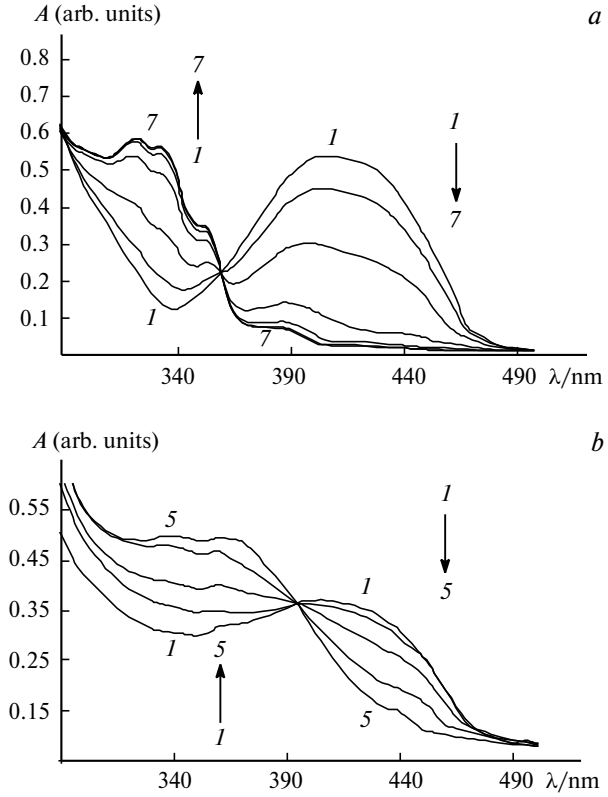
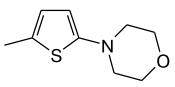


Fig. 13. *a*. Electronic absorption spectra of compounds **37a** before (*1*) and after (*2*—*7*) irradiation with light at $\lambda > 400$ nm in carbon tetrachloride ($C = 4 \cdot 10^{-5}$ mmol L^{-1}). *b*. Electronic absorption spectra of compound **37a** in CCl_4 (*1*), CCl_4—DMF, 6 : 1 (*2*), CCl_4—DMF, 4 : 1 (*3*), CCl_4—DMF, 1 : 4 (*4*), and DMF (*5*).

Table 3. Absorption band maxima and molar absorption coefficients in the electronic absorption spectra of compounds **37**—**40** in CCl_4

Compound	R^1	R^2	λ/nm	ε/L mol^{-1} cm^{-1}
37a	Ph	*p*-$MeOC_6H_4$	415	15430
37b	*p*-MeC_6H_4		425	24680
37c	*p*-FC_6H_4		395	10460
37d	*p*-$NO_2C_6H_4$		425	24680
37e	*p*-$MeOC_6H_4$		410	10820
37f	*p*-MeC_6H_4	3,5-di(OMe)C_6H_3	424	2020
37g	*p*-FC_6H_4		410	2800
37h	*p*-$NO_2C_6H_4$		438	19900
37i	*p*-FC_6H_4	*p*-$Me_2NC_6H_4$	405	8110
37k	*p*-$MeOC_6H_4$		417	10370
37l	Benzothiazol-2-yl	*p*-$MeOC_6H_4$	398	19720
38a	Ph	*p*-$MeOC_6H_4$	400	17550
38b	*p*-FC_6H_4		403	14110
38c	*p*-$MeOC_6H_4$		399	6700
38d	*p*-FC_6H_4		401	14690
38e	*p*-$MeOC_6H_4$		400	12240
39	Ph	Ph	390	57180
40	Ph	Ph	365	15990

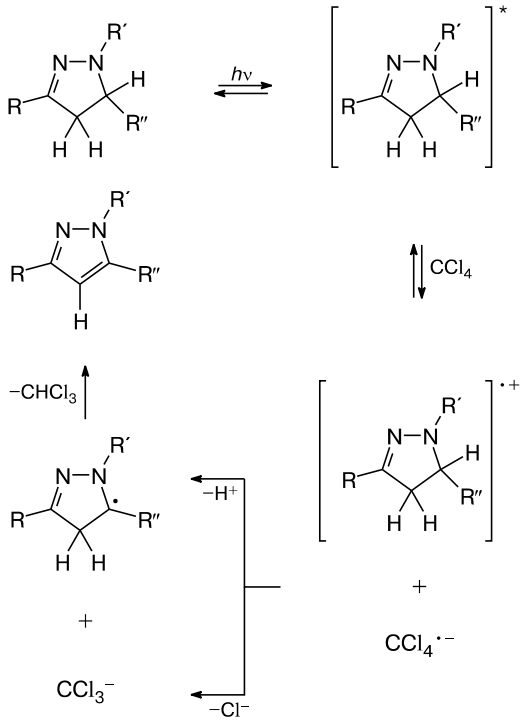
A decrease in the intensity of the signals from pyrazoline (δ 5.2, 4.3, and 3.4) and the appearance of a signal at δ 7.2 are observed with time in the ^{1}H NMR spectra. The resulting ^{1}H NMR spectrum completely coincides with the spectrum of pyrazole obtained by the oxidation of the initial pyrazoline with sodium bichromate. After evaporation of the solution, the corresponding pyrazole was isolated in a quantitative yield.

The relative rates for photodehydrogenation of pyrazolines **37**—**40** in carbon tetrachloride (the values of k_{rel} were calculated with respect to pyrazoline **37a**) and their ionization potentials (I/eV) and electron affinities (EA) are given in Table 4. It was reasonable to assume that the values obtained for relative photodehydrogenation rates would correlate with the ionization potentials of substituted pyrazolines, since they should undergo photoionization and can donate an electron from the ground state to the CCl_4 molecule. However, the correlation coefficient of logarithms of k_{rel} with the ionization potentials was poorly satisfactory. We found that the relative photodehydrogenation rate also unsatisfactorily correlate with the values of electron affinity of pyrazolines. This correlation could be expected if assuming that pyrazolines can undergo photoaromatization from the excited state. It should be noted that the values of ionization potentials and electron affinity were calculated by several semiempirical methods, and well consistent results were obtained.

Based on the aforesaid, we proposed the following scheme of the discovered reactions of pyrazoline photodehydrogenation (Scheme 25). It is seen that a considerable contribution to the photodehydrogenation can be made by transformations of radicals. In this case, it is not surprising that the relative rate constants for the reaction discussed do not correlate with the values of both ionization potentials and electron affinity.

The discovered conversion of aryl(hetaryl)pyrazolines has analogies in the heterocyclic series, however, under more drastic UV irradiation. In particular, the specific influence of CCl_4 was reported for the dehydrogenation of

Scheme 25



Hantzsch 1,4-dihydropyridines, which in CCl_4 or in a CCl_4—MeCN mixture were irradiated with a high-pressure mercury lamp with a power of 250 W.[67] It was found that the photodehydrogenation of dihydropyridines to pyridines upon irradiation is accompanied by the formation of chloroform and an increase in acidity of the medium. Unlike the scheme discussed in literature, we do not assume the direct electron transfer from the non-excited pyrazoline molecule to the CCl_4 molecule. At the first step, pyrazoline transits, most likely to the excited state, after which the electron transfer from the excited pyrazoline molecule to CCl_4 occurs. The $CCl_4^{\cdot -}$ radical anion is very unstable and, hence, rapidly dissociates to the trichlo-

Table 4. Relative rate constants for photodehydrogenation (k_{rel}) and calculated ionization potentials (I) and electron affinities (EA) for compounds **37**—**40**

Compound	k_{rel}	I /eV	−EA /eV	Compound	k_{rel}	I /eV	−EA /eV
37a	1.00	8.266	1.167	**38k**	2.300	8.011	1.099
37b	2.51	8.177	1.160	**38l**	0.016	8.325	1.354
37c	1.81	8.331	1.244	**38a**	2.850	8.067	0.884
37d	0.01	8.312	1.385	**38b**	2.560	8.142	0.957
37e	1.50	8.109	1.153	**38c**	4.720	7.942	0.868
37f	1.90	8.156	1.137	**38d**	2.010	8.145	0.968
37g	2.73	8.012	1.052	**38e**	2.910	7.973	0.883
37h	0.07	8.578	1.371	**39**	3.460	8.160	0.245
37i	0.83	8.212	1.840	**40**	0.840	8.067	0.465

romethyl radical and chloride ion. The pyrazoline radical cation formed eliminates the proton and, interacting with the trichloromethyl radical, transforms into pyrazole. According to this scheme, the aryl(hetaryl)pyrazoline molecule first plays as a sensitizer of CCl_4 destruction and in the subsequent steps acts as a proton source.

It has previously been published that a CCl_4 molecule can act as an electron acceptor (Scheme 26). Accepting an electron, this molecule forms an unstable radical anion that decomposes very rapidly to eject the trichloromethyl radical capable of eliminating the hydrogen atom from the corresponding substrate. In turn, the chloride ion can act as a proton acceptor.[68,69]

Scheme 26

$$CCl_4 + e \rightleftharpoons CCl_4^{\cdot -} \longrightarrow {}^{\cdot}CCl_3 + Cl^-$$

A specific feature of the process shown in Scheme 25 is proton detachment during irradiation of aryl(hetaryl)-coumarin. An increase in acidity of the medium during photodehydrogenation was revealed in a direct experiment: irradiation of aryl(hetaryl)coumarin in a CCl_4 solution increases the concentration of the protonated form of Thymol blue indicator in a range of 500 nm (Fig. 14).

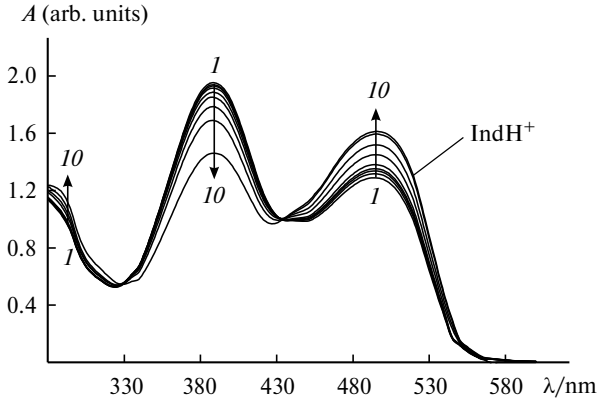
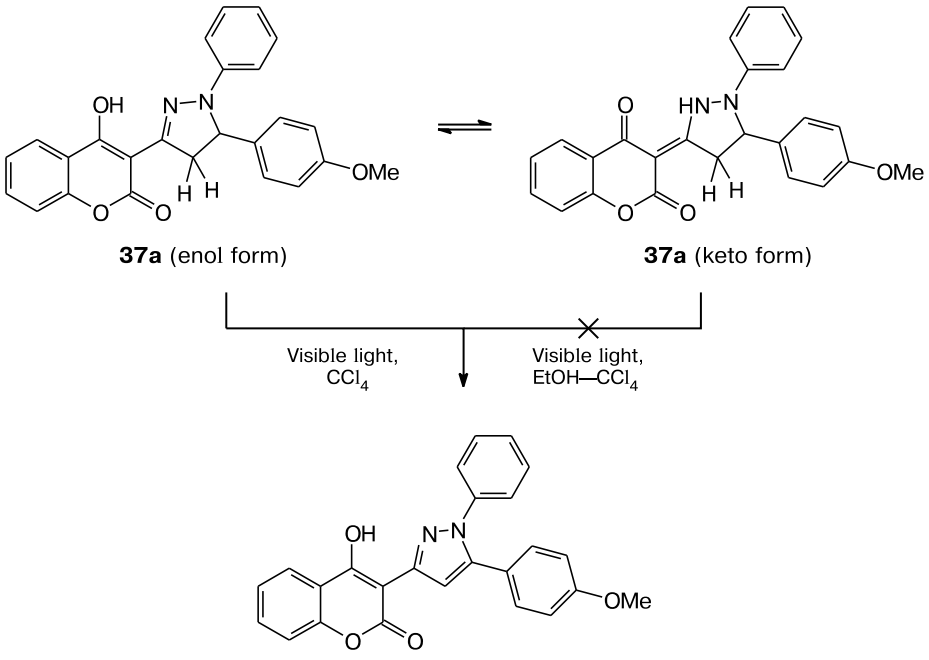


Fig. 14. Electronic absorption spectra of 1,3,5-triphenylpyrazole **40** with indicator Thymol blue before (*1*) and after (*2—10*) irradiation with visible light in the presence of carbon tetrachloride.

As mentioned above, 4-hydroxycoumarin derivatives are very prone to tautomerism. We found that 4-hydroxy-3-pyrazolinylcoumarins are not exception and are also prone to tautomeric transitions as the solvent composition changes.[25] What is the role of tautomeric transformations in the observed reaction of photodehydrogenation of 1,3,5-triaryl(hetaryl)pyrazolines? It turned out that (under other equivalent conditions) photodehydrogenation occurs efficiently only when aryl(hetaryl)pyrazoline is in the enol form. Photodehydrogenation nearly does not occur in the presence of ethanol that favors the transition of aryl(hetaryl)pyrazoline to the keto form (Scheme 27).

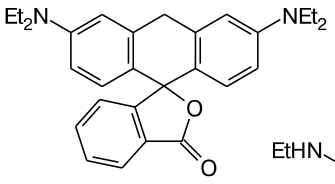
Other examples of the influence of the tautomeric form on the functional properties of coumarin derivatives and its analogs should be mentioned.[70—75] We established, in

Scheme 27

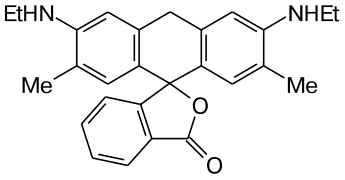


particular, that the cinnamoyl derivatives of dehydroacetic acid exhibit pronounced inhibitory properties with respect to HIV-1 integrase acting at the stage of both 3´-processing and chain transfer. It is important that, according to the computer screening data, the tautomeric form is a significant factor of the presence of pharmacological properties of the organic substrate in this case as well.[70,71]

We established the photoacidic properties of aryl(hetaryl)pyrazolines and studied in detail the conditions of their application for the generation of fluorescence of lactone forms of two rhodamine dyes, Rhodamine B and Rhodamine 19, in order to develop new optical media for data recording with fluorescence read-out.



Rhodamine B
(λ^{fl}_{max} = 560 nm)



Rhodamine 19
(λ^{fl}_{max} = 587 nm)

The optimum results were obtained for pyrazolines **37a** (λ_{max} = 405 nm) and **40** (λ_{max} = 385 nm). The changes in the absorption and fluorescence spectra of pyrazoline **37a** in a CCl_4 solution upon irradiation are shown in Fig. 15.

It turned out that aryl(hetaryl)pyrazolines also work as photoacids in the polymer films (Fig. 16). Irradiation of the poly(methyl methacrylate) (PPMA) film with dissolved pyrazoline **37a**, hexachloroethane, and Rhodamine B with light in the wavelength range from 360 to 400 nm results in

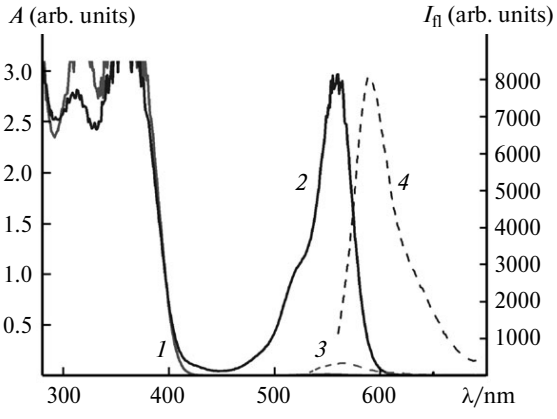


Fig. 15. Absorption (*1*, *2*) and fluorescence emission spectra (*3*, *4*) of pyrazoline **37a** in a CCl_4 solution in the presence of Rhodamine B before (*1*, *3*) and after (*2*, *4*) irradiation through the ZhS-10 light filter.

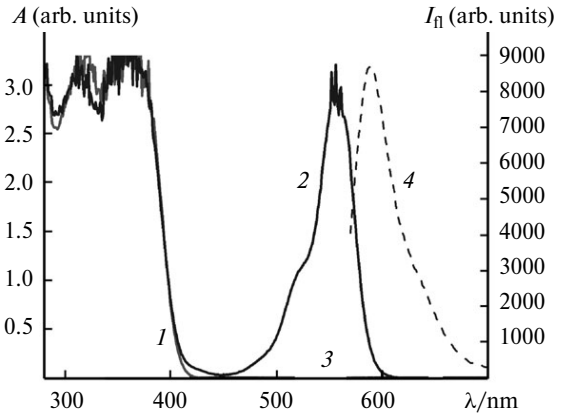


Fig. 16. Absorption (*1*, *2*) and fluorescence emission spectra (*3*, *4*) of the PMMA film containing Rhodamine B, pyrazoline **37a**, and hexachloroethane before (*1*, *3*) and after (*2*, *4*) irradiation through the ZhS-10 light filter. Curve *3* coincides with the abscissa.

film dyeing and the appearance of fluorescence. As in the case of a carbon tetrachloride solution, the irradiation of a poly(methyl methacrylate) film containing a mixture of Rhodamine B and hexachloroethane through the same light filter does not change the spectral characteristics.

The new photosensitive optically transparent polymer material containing the CCl_3 or CBr_3 groups in the polymer chain and including Rhodamine B or Rhodamine 19 as a fluorescent precursor was synthesized as a result of the study performed. The material is suitable for optical data storage with fluorescence read-out.[76,77]

Coumarin and its analogs containing the hydroxy and acyl groups in the lactone (lactam) ring belong to the series of heterocyclic β,β-tricarbonyl derivatives with the π-electronic structure, high reactivity and ability to diverse isomerization transformations, which make them very promising in synthesis of new functional compounds capable of structural changes under the influence of various factors: irradiation, change in the pH of the medium, solvent composition, and the presence of a bioorganic substrate and metal ions. The target functional materials are interesting for the production of materials for optoelectronics and sensor systems, including those capable of detecting the corresponding effect by the change in fluorescence.

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