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SPIROPYRANS: SYNTHESIS, PROPERTIES, AND APPLICATION. (REVIEW)*

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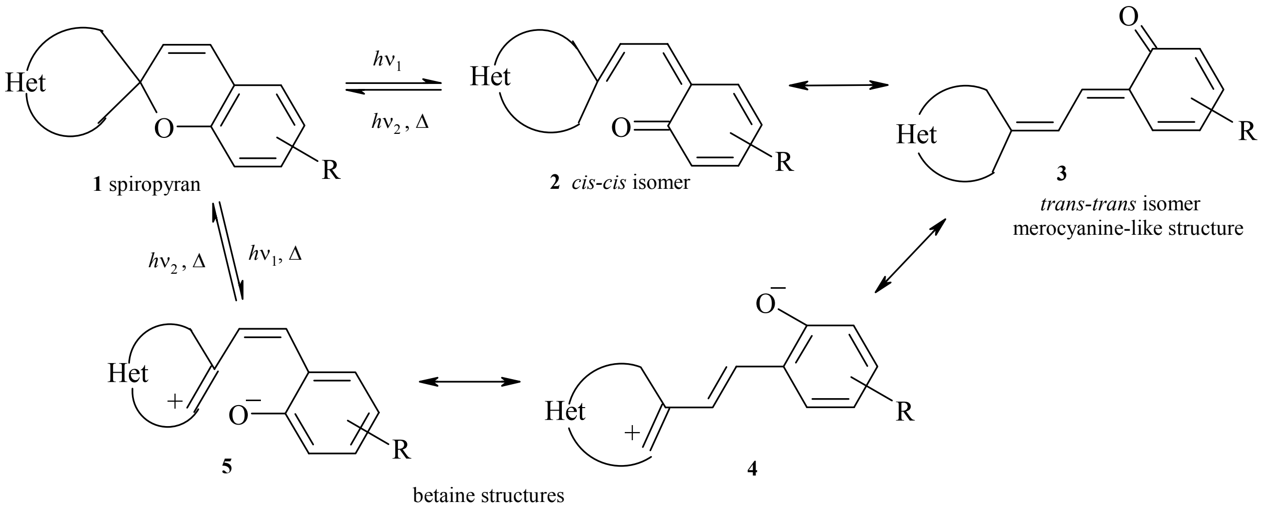
Published data on the synthesis and structural modification of spiropyrans and bisspiropyrans and production of the heteroanalogs of spiropyrans are classified and analyzed. The chemical characteristics of spiropyrans, including complexation of the open-chain isomers and cyclic forms are examined. Special attention is paid to the photochromic characteristics of spiropyrans at interfaces between phases.

Keywords: bisspiropyrans, light-sensitive materials, spiropyrans, photochromism.

The number of scientific and technical developments in which new silver-free light-sensitive materials have been produced has increased vigorously over recent years. This is due to many reasons, including the fact that the demand for silver for technical purposes throughout the world has increased with a simultaneous tendency for its production to lag behind on account of the exhaustion of world resources. Photochromic materials capable of changing color under the influence of activating radiation with various spectral make-up are finding ever increasing application. An important class of organic photochromes at the present time is the spiropyrans **1**, which are capable of forming colored quinoidal betaine structures **2-5** that rearrange reversibly to the initial spiro forms under the influence of visible light or spontaneously.



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* Dedicated to our tutor Academician V. I. Minkin on the occasion of his 70th birthday.

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Wide interest in the spiropyrans, which have been known since the beginning of the twentieth century [1], appeared in the middle of the twenties, when their reversible thermochromic properties were discovered [2-4], and it increased greatly as their photochromic properties became known [5]. The results of investigations into the structure and characteristics of spiropyrans largely up to 1980 have been discussed and analyzed in existing reviews and monographs [6-16], and they have been partly supplemented by more recent results [17, 18].

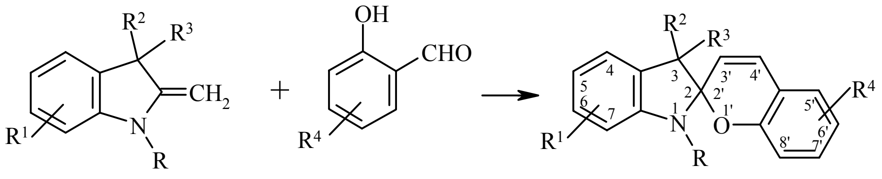
In the present review the principal methods for the production of spiropyrans and certain new aspects of their modification and also their unusual chemical and photochromic applications are examined in detail.

1. SYNTHESIS AND STRUCTURAL MODIFICATION OF SPIROPYRANS

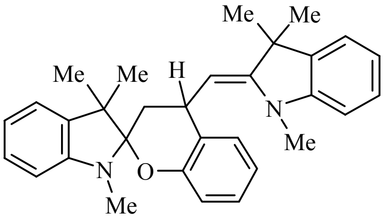
The standard methods for the synthesis of spiropyrans remain practically unchanged and can be divided into two main groups: 1) Condensation of methylene bases (or their precursors) with *o*-hydroxy aromatic aldehydes; 2) condensation of *o*-hydroxy aromatic aldehydes with the salts of heterocyclic cations containing active methylene groups, isolation of the intermediate styryl salts, and subsequent removal of the elements of the acid.

1.1. Production of Spiropyrans by Condensation of Methylene Bases with *o*-Hydroxy Aromatic Aldehydes

This method is characteristic of the synthesis of spiropyrans of the indoline series **7**, the method for the preparation of which remains practically unchanged from the time of the classical paper of Wizinger [19], i.e., boiling the methylene bases of nitrogen heterocycles (for spiropyrans of the indoline series – the Fischer base **6**) and *o*-hydroxy aromatic aldehydes in suitable solvents (most often in alcohol). In some cases it is convenient to conduct the reaction in DMF [20]. In the proposed form, however, this reaction often leads to side products of the type **8**, the formation mechanism of which was discussed in detail in the review [14].



6 **7**



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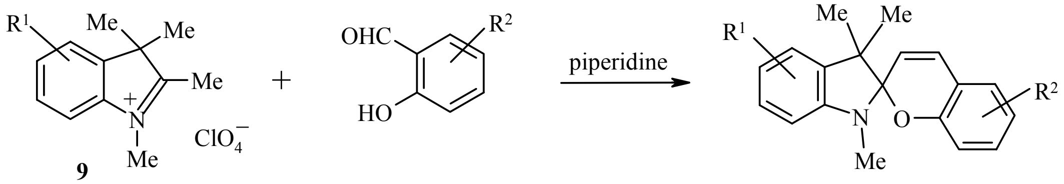
In order to reduce the yield of the "dicondensed" side product it is recommended to use the corresponding quaternary indolenylium salt **9** in a mixture with an equimolar amount of an organic base (most often piperidine) instead of the methylene base.

Key: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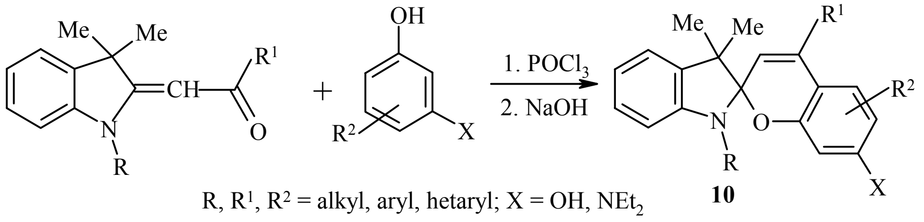
A large amount of indolinochromenes was produced by the condensation reactions of indoline bases or their salts with *o*-hydroxy aromatic aldehydes [20], but it was only possible to obtain spiropyrans of the indoline series of type **10**, containing substituents at position 4', according to the following scheme [21-23]: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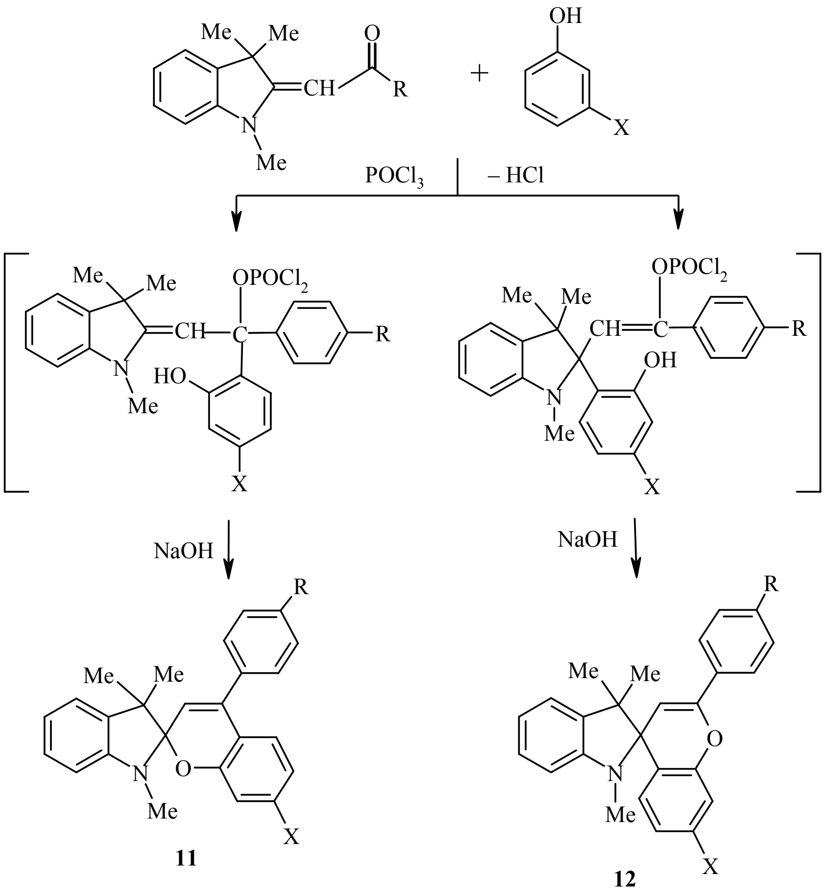
R, R^1, R^2 = alkyl, aryl, hetaryl; X = OH, NEt_2

Study of this reaction for the case of resorcinol showed that the presence of two reaction centers in the acyl derivative of the Fischer bases resulted in a mixture of [2H-1] (**11**) and [4H-1] (**12**) benzopyrans, the ratio of which depended on the nature of the solvent and the substituent X [24].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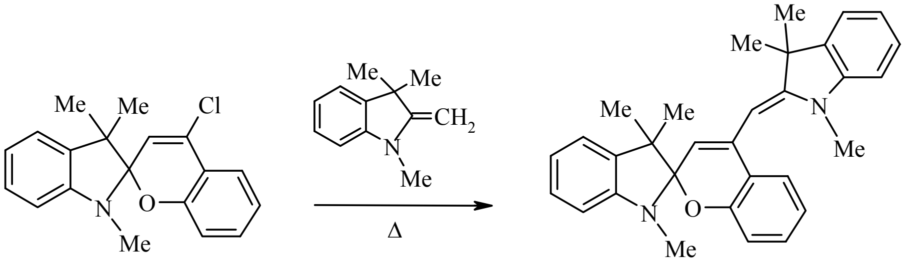
12

R = H, OMe; X = OH, NEt_2

By the reaction of 3-(R-2-hydroxyphenacylidene)-1,3,3-trimethylindolines with phosphorus oxychloride it is possible to obtain 4'-Cl-substituted indolinospiropyrans **13**, the heating of which with a Fischer base leads to structures **14**, containing an indolenine residue at position 4' [25].



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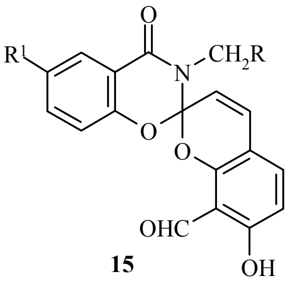
14

The development of effective methods for the synthesis of certain *o*-hydroxy aromatic aldehydes made it possible to obtain new photochromic indoline spiropyrans containing formyl [26], benzoyl, carboxyl, hydroxymethyl, alkyl, nitro [27], and halogen [28] substituents and nontraditional π-accepting substituents [29]. It was also possible to obtain spiropyrans exhibiting liquid crystal characteristics [30], optically active spiropyrans containing a tolane substituent [31], and also spiropyrans containing a fullerene fragment [32].

Spiropyrans of the benzoxazinone **15** and indoline **16** series based on 2,4-dihydroxyisophthalaldehyde and containing *ortho*-located hydroxy and formyl groups in the benzo nucleus of the [2H]chromene fragment were obtained [33].



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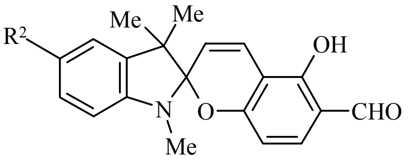

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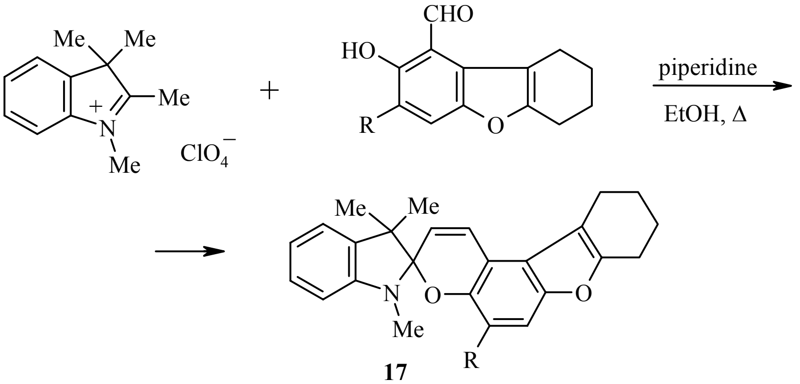
R = H, Ph; R^1, R^2 = H, Cl

New indolinospirochromenes **17** containing a condensed furan fragment (a unique analog of a π-donor substituent) at position 6' in the chromene part of the molecule were synthesized (R = H [34], R = Br [35]).



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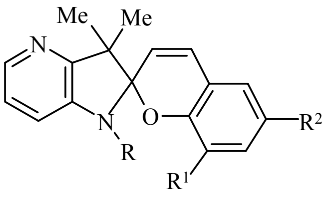
By using new analogs of 1,3,3-substituted 2-methyleneindolines it was possible to obtain spiropyrans with alkyl, benzyl, cyclohexyl [36], and glucoside [37] groups and also substituents containing crown ether components at the nitrogen atom [38].

Spiropyrans **18-21** containing a condensed pyridine fragment were obtained in a similar way [39-41], but the synthesis of the first spiropyrans based on thieno[3,2-*b*]pyrrole **22** only became possible in 2003 [42].



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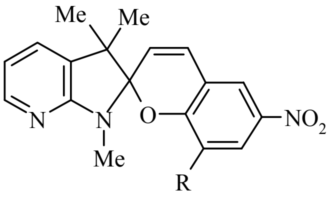

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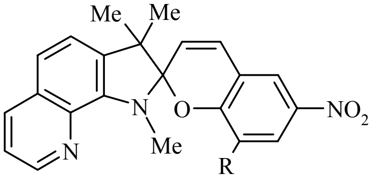
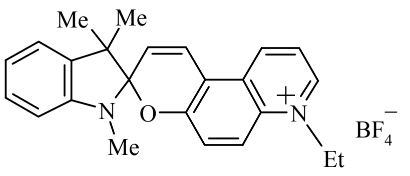


20

18 R = Me, Et, R^1, R^2 = H, NO_2, Hal; **19** R = H, OMe, Br; **20** R = H, Me, Br



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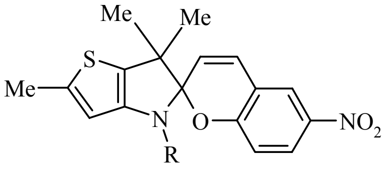

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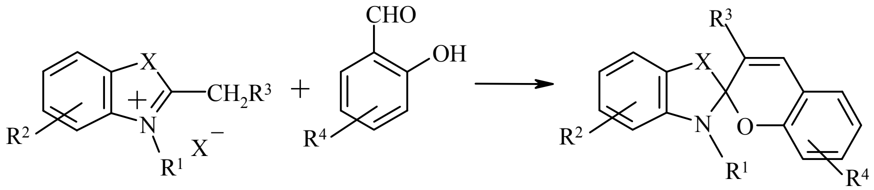
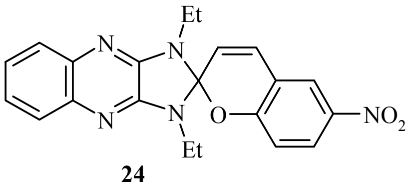
Spiropyrans with the general formula **23** (X = O [43], X = S [44], X = Se [45], X = NR [46]) were obtained by boiling the respective benzazolium salts with *o*-hydroxy aromatic aldehydes in the presence of piperidine or pyridine.



23

Published data on the mechanism of formation of these spiropyrans and the effects of the medium, solvent, the nature of the anion X^- in the quaternary salt, and the substituents on their yields were analyzed in detail in the review [14].

Spiropyrans **24** based on imidazoquinoxaline [47] and spiropyrans of the benzisoxazoline series **25** [48] augment the benzazole spiropyran group.



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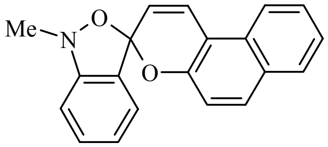

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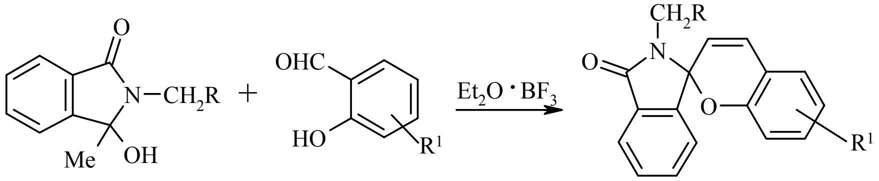
An original single-stage method for the production of azaindane spiropyrans **26** by the condensation of substituted salicylaldehydes with 1-hydroxy-1-methylisoindolin-3-one (a unique precursor of the respective methylene bases) in diethylene glycol was developed using complexes of boron as catalysts [49].

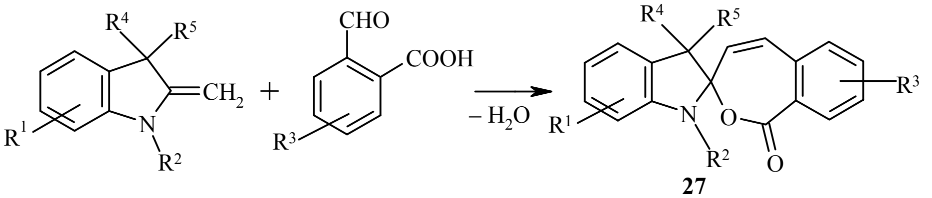


R = H, Ph

26

Papers on the synthesis of spiropyrans based on six-membered nitrogen heterocycles with one nitrogen atom were reviewed in [14]. Spiropyrans of the quinoline, isoquinoline, and 3,4-dihydroisoquinoline series and also their benzannelated analogs (spiropyrans of the phenanthridine, acridine, and diazapyrene series) were obtained.

Attempts to modify the structure of indoline spiropyrans by the synthesis of compounds containing a seven-membered ring instead of a six-membered pyran ring led to the spirooxepinones **27** [50]. They were, however, unsuccessful when 8-hydroxy-1-naphthaldehyde was used for the production of a derivative without the carbonyl group.



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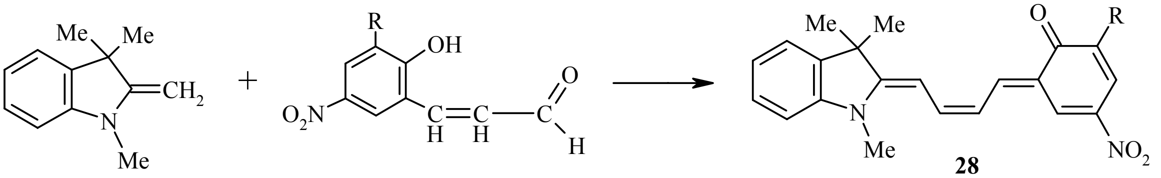
It was not possible to obtain compounds containing an eight-membered ring either in the reactions of the vinylogs of the Fischer base with salicylaldehydes or in the reaction of the Fischer base with *o*-hydroxycinnamaldehydes [51-53]; in rare cases only the open-chain forms of spirooxacins **28** can be obtained [54].

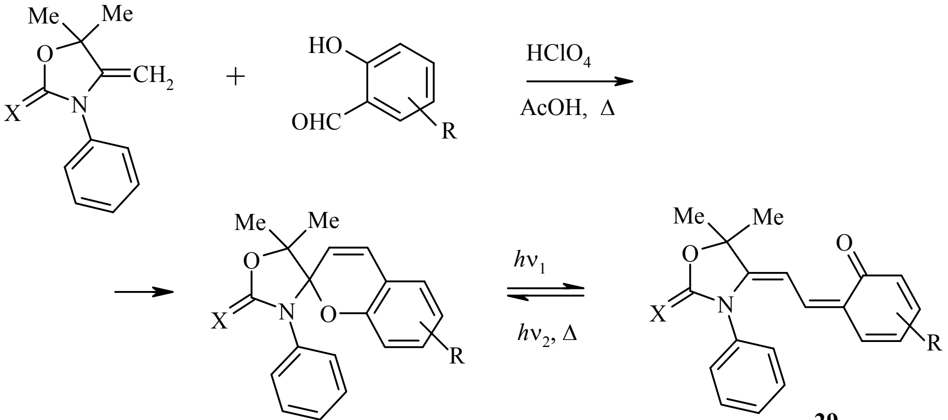


28

R = Br, NO_2

The previously rarely encountered class of spiropyrans (derivatives of mononuclear heterocycles [55, 56]) was significantly extended owing to a cycle of papers [57-60] on the synthesis of spiropyrans based on saturated azaheterocycles.

By condensation of the stable methylene bases of 5,5-dimethyl-4-methylene-2-oxo(thioxo)-3-phenyl-1,3-oxazolidines with *o*-hydroxy aromatic aldehydes in acetic acid in the presence of catalytic amounts of perchloric acid it was possible to obtain the corresponding photochromic spiropyrans **29** with yields of 60-70% [61-63].



X = O, S

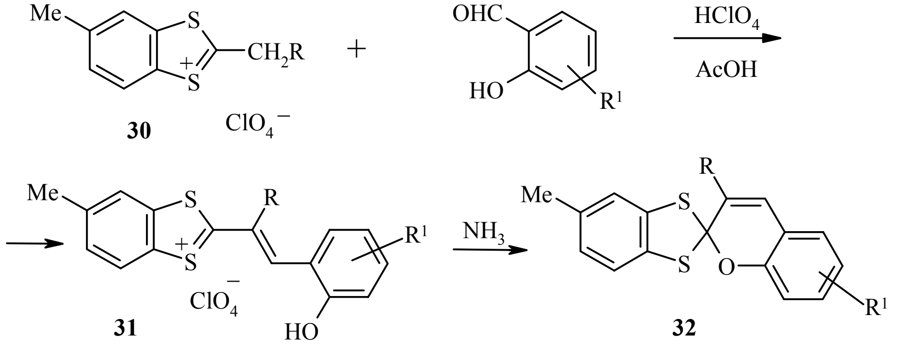
29

R = H, 5',6'-benzo, 6',7'-benzo, 7',8'-benzo, 6'-Me, 6'-NO_2, 8'-NO_2, 6'-OMe, 8'-OMe, 7'-OH, 6'-Cl, 6',8'-Cl_2, 6'-Br, 6',8'-Br_2, 6'-Br, 8'-NO_2, 6'-NO_2, 8'-Br

1.2. Production of Spiropyrans by Condensation of *o*-Hydroxy Aromatic Aldehydes with Salts of Heterocyclic Cations Containing Active Methylene Groups, Isolation of the Intermediate Styryl Salts, and Removal of the Elements of the Acid

The standard procedure in this case is condensation of *o*-hydroxy aromatic aldehydes with the salts of heterocyclic cations followed by removal of the elements of the acid from the obtained styryl salt with organic bases (gaseous ammonia or amines).

Spiropyrans of general type **32** were synthesized in a similar way by condensation of 2,5-dimethyl- and 2-ethyl-5-methylbenzo-1,3-dithiolium perchlorates **30** with substituted aromatic *o*-hydroxybenz(naphth)-aldehydes with heating for 5-10 min in acetic acid at 90-100°C with a catalytic amount of perchloric acid (with isolation of the styryl salt **31**) [64]. The styryl derivatives **31**, obtained with yields of 60-80%, are deeply colored crystalline substances. The elimination of the elements of perchloric acid from them, leading to the spiropyrans **32**, is achieved with the highest yields by treatment of the derivatives **31** with a ether or benzene solution of dry ammonia.



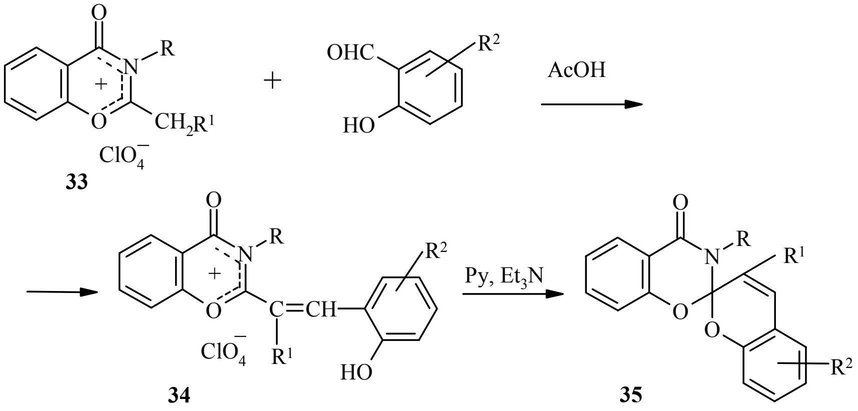
30

31

32

R = H, Me, R^1 = H, 5',6'-benzo, 7',8'-benzo, 6'-NO_2, 8'-NO_2, 8'-OMe, 6'-Cl, 6'-Br, 7'-NEt_2

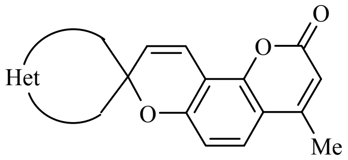
The research team at Rostov State University developed an original two-stage procedure for the synthesis of spiropyrans of the benzoxazinone series with preparative isolation of the styryl salt **34**, the *trans* structure in the vinyl fragment of which was proved by ^{1}H NMR spectroscopy. Subsequent removal of the elements of perchloric acid from compounds **34** by tertiary amines (triethylamine or pyridine) led to the spiropyrans **35** [65].



R = H, Me, *i*-Pr, CH$_2$Ph; R^1 = H, Me, R^2 = H, OMe, 5,6-benzo

The choice of tertiary amines for removal of the elements of perchloric acid was based on the high reactivity of the benzoxazinonium cation toward ammonia and primary and secondary amines [66].

Spiropyrans of the coumarin series **36** were obtained by a combination of all the above-mentioned methods of synthesis using 8-formyl-7-hydroxy-4-methylcoumarin as aldehyde component [67].



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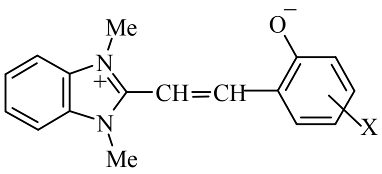
Het = 1-alkyl-3,3-trimethylindolenyl; 5,5-dimethyl-2-oxo-3-phenyloxazolidenyl; 3,3-dimethyl-2-oxaindenyl; 3-methyl-2H-1-benzopyrenyl; 3-methyl-2H-1-[2,1-*a*]naphthopyrenyl; 1,3-dithiolenyl; 5-methylbenzo-1,3-dithiolenyl

Sometimes only the anhydro bases **37** were obtained instead of the expected spiropyrans [46, 68]. According to the authors, this was due to the low electrophilicity of the mesocarbon atom of the imidazole ring [46]. An increase in the electrophilicity achieved by the introduction of π-accepting substituents into the benzene ring of the benzimidazole fragment led to stabilization of the spiropyran structures **38** even in the absence of substituents at position 3'. Here the anhydro bases **37** that were formed were converted into the spiropyran structures **38** by boiling in aprotic solvents [46].



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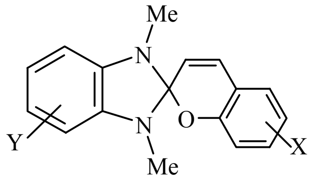

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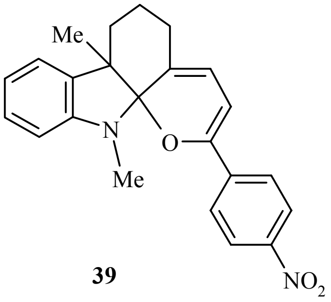
37 X = H, 5-NO$_2$, 3,5-Br$_2$, 5,6-benzo; **38** X = H, Y = 5-NO$_2$; X = H, Y = 5,6-(NO$_2$)$_2$; X = 6'-OMe, Y = 5,6-(NO$_2$)$_2$

A quantum-chemical approach was applied to the problems of predicting the stability of spiropyran structures and the displacement of the merocyanine↔spiropyran equilibrium to one or the other side using MO methods in the SCF-MO PPP approximation for a wide range of heterocycles and spiropyrans. According to the obtained data, a preference for spiropyran structures can be expected for heterocyclic cations with energies of anionic localization $L_\alpha^- \leq 6.19$ eV and for merocyanine structures with $L_\alpha^- > 6.39$ eV. The effect of substituents in the benzopyran part was analyzed, and it was shown in particular that 6,7-benzannelated derivatives are systems that are most stable in the spiropyran form [69]

Whereas it is relatively easy to obtain spiropyran derivatives of mononuclear heterocycles [55-60], it was for a long time impossible to obtain "monocyclic" spiro compounds of another type – spiro[2H]pyran – on account of their tendency to exist in the merocyanine form [70].

Only by appropriate choice of structural factors stabilizing the spiro form was it recently possible to synthesize the indoline derivative **39**. The absence of photochromic characteristics in this compound provided the basis for the conclusion that the coupling of the pyran ring with the aromatic ring is an essential condition for the appearance of photochromism [71].



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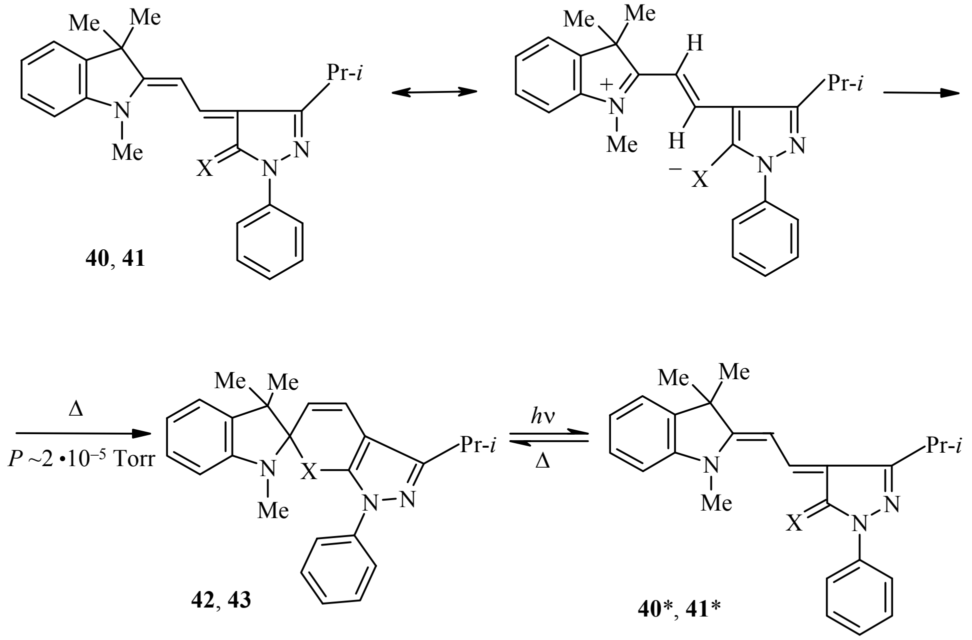
It is possible to overcome the difficulties arising during the formation of the anhydro bases in the synthesis of spiropyrans by using isomerization of the merocyanine structures to spiropyran structures during vacuum deposition of the merocyanines onto a solid support (quartz, glass, potassium bromide plates) [72]. The polydisperse film formed in this process (evaporator heating temperature 450°C) is colorless and contains the cyclic 2H-thia(selena)pyran form [73].

The method for the "solid-phase" synthesis of spiro compounds developed at the Scientific-Research Institute of Physical and Organic Chemistry of Rostov State University makes it possible to obtain spiro compounds in cases where the energy of the ground state of the merocyanine isomer is lower than that of the cyclic isomer and the standard methods of production are unsuccessful. In this way it is possible to synthesize stable "monocyclic" analogs of spiro[2H]pyrans [74, 75].

It was not possible to obtain 1',3',3'-trimethylspiro[2H-1-(3-isopropyl-1-phenylpyrazolo)[4,5-*e*]thiapyran-2,2'-indoline] (**42**) and 1',3',3'-trimethylspiro[2H-1-(3-isopropyl-1-phenylpyrazolo)[4,5-*e*]selenapyran-2,2'-indoline] (**43**) by the usual methods (boiling in aprotic solvents by analogy with the cyclization of merocyanines of the benzimidazole series [68]). Cyclization only takes place under the conditions of thermal vacuum deposition of the respective merocyanine 5-isopropyl-2-phenyl-4-[2-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)ethylidene]-2,4-dihydropyrazole-3-thione (**40**) or 5-isopropyl-2-phenyl-4-[2-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)ethylidene]-2,4-dihydropyrazole-3-selenone (**41**) onto a cooled surface [73-75].



40, **41**

42, **43**

40*, **41***

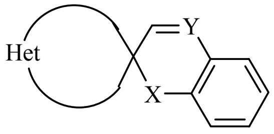
40, **40***, **42** X = S, **41**, **41***, **43** X = Se

Here the "open" merocyanine form is fully converted into the "closed" spiropyran form. The proposed method opens up the possibility of obtaining spiro compounds for those cases where the energy of the ground state of the open-chain isomer is lower than that of the cyclic isomer.

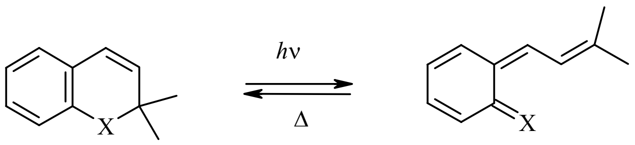
During UV irradiation compound **42** is converted into the "activated" open form **40***, which can be transformed into compound **42** under the conditions of the reverse dark reaction.

2. PRODUCTION OF THE HETEROANALOGS OF SPIROPYRANS

Heteroanalogs of spiropyrans known at the present time include spirooxazines (X = O, Y = N) and the isologs of spiropyrans (X = O, Y = C), spirothia(selena)pyrans (X = S, Se, Y = C), with the general formula:

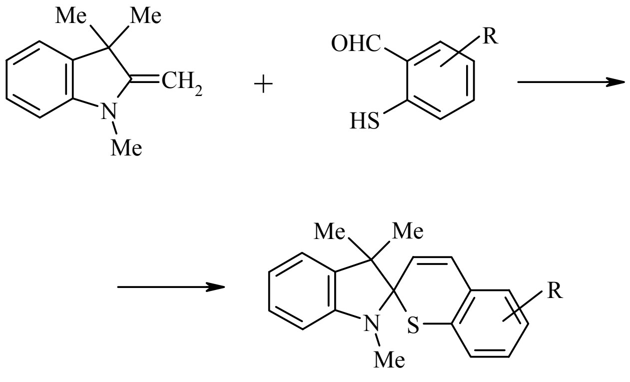


In this review we will dwell in greater detail on the spirothia(selena)pyrans. The interest in such compounds is due primarily to the fact that it was shown during investigation of the photochromic properties of [2H]chromenes (X = O) and their isologs [2H]thiachromenes (X = S) and [2H]selenachromenes (X = Se) that replacement of the oxygen by sulfur and selenium leads to a strong bathochromic shift of the long-wave absorption band of the open photoinduced form.



During a comparative study of the absorption spectra of chromenes [76], thiachromenes [77], and selenachromenes [78] before and after standard irradiation for 25 min with light having λ_{max} 313 nm at 77 K in a vitrifying solvent (5:2 isopentane–2-propanol) at $c \sim 10^{-4}$ M with $l = 1$ cm it was shown that variation of the heteroatom has little effect on the absorption spectra of the colorless cyclic forms. In the colored photoinduced forms, however, the transition from O to S leads to a bathochromic shift of up to 100 nm. The long-wave band in the absorption spectrum of the photoinduced form of selenachromene lies in the region of 660 nm and is strongly shifted bathochromically in relation to the corresponding absorption band of chromene (470 nm).

The thiaspiropyrans **44**, which are heteroanalogs of indolinospirochromenes in which the oxygen in the pyran ring is substituted by sulfur, are obtained by boiling the Fischer bases and thiosalicylaldehydes in methanol [79, 80]. These compounds have a strong bathochromic shift of the long-wave absorption band for the colored form compared with the oxygen-containing analogs.

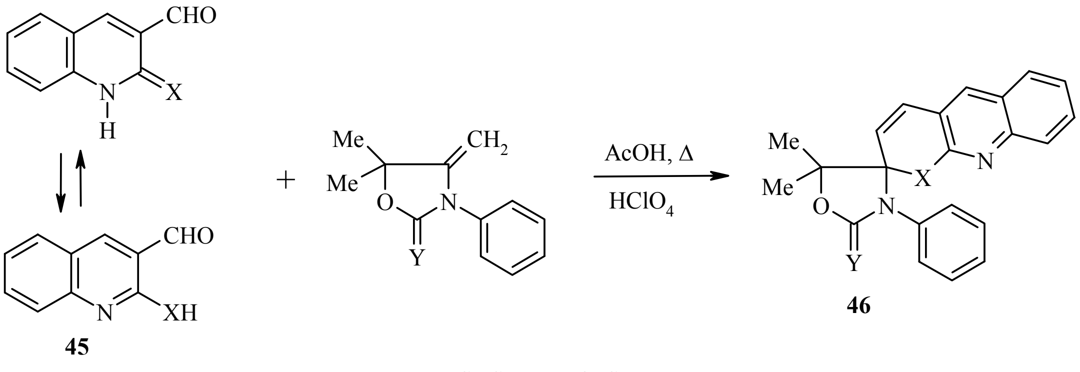


44

A method was developed for the production of thiaspiropyrans **44** by boiling quaternary indolenylium salts, thiosalicylaldehydes, and piperidine in ethanol [81].

The preparation of spiroselenapyrans is difficult on account of the lack of stable selenasalicylaldehydes but nevertheless proved possible with 3-formyl-2-(1H)quinolineselenone **45** (X = Se) as aldehyde component [82].

Spirothiapyrans **46** (X = Se), containing a condensed quinoline fragment, were also obtained in a similar way [83].



45

46

X = S, Se; Y = O, S

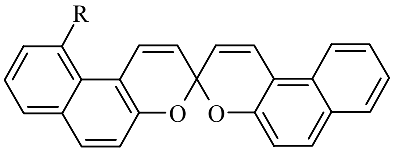
The accumulated synthetic and theoretical experience and also all the increasing technical demands of spiropyrans (the bathochromic shift of the absorption band of the open form and the increased life time of the colored form) have prompted scientists to synthesize structures containing more than one center, since according to the theory of conjugated chromophores an improvement in the spectral characteristics can be expected.

In recent decades a series of bisspiropyrans and compounds containing more than one spirocyclic center have been synthesized. However, no serious analysis of the obtained results has been undertaken.

3. SYNTHESIS AND CHARACTERISTICS OF BISSPIROPYRANS

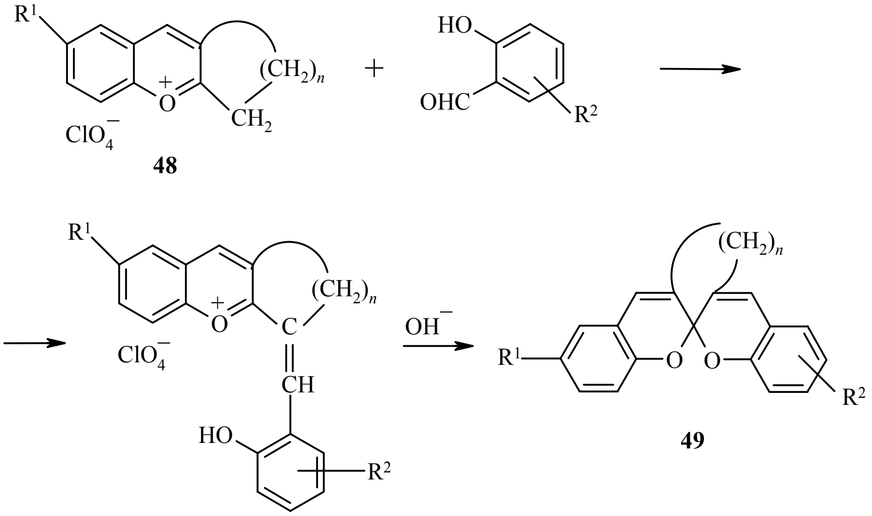
Bisspiropyrans are of particular interest in connection with the fact that during possible simultaneous opening of two pyran fragments the conjugation chain is significantly increased, and the maximum of the absorption band of the photoinduced form should undergo a strong bathochromic shift. The classical method for the synthesis of spirobipyrans by the condensation of aromatic *o*-hydroxy aldehydes with ketones has been improved in recent years in both the single-stage and the two-stage (with the intermediate isolation of the *o*-hydroxystyrylpyrylium salt) modifications.

Typical representatives of bisspiropyran systems are the spirodinaphthopyrans **47** [19, 84], in which two naphthopyran fragments are linked through a spirocarbon atom.

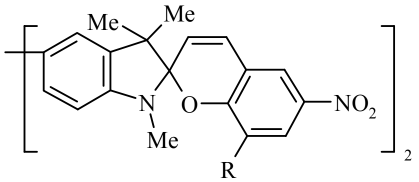


47

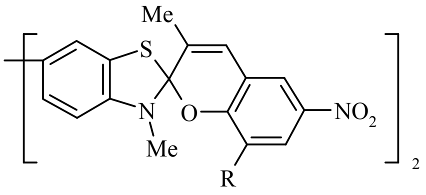
Starting from the pyrylium salt **48** an interesting analog of spirodinaphthopyrans **49** was obtained, and its method of synthesis provides the possibility of producing unsymmetrical bisspiropyrans [85].



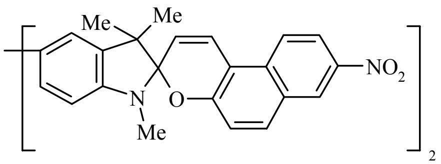
Bisspiropyrans in which the two spiropyran fragments are linked to each other by a simple σ-bond in the hetarene **50-52** or benzopyran **53** component were obtained [86].



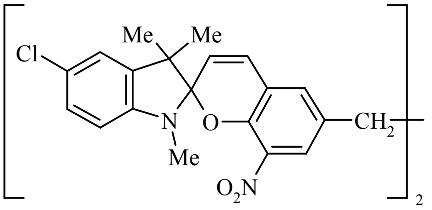
50 R = H, OMe



51 R = H, OMe

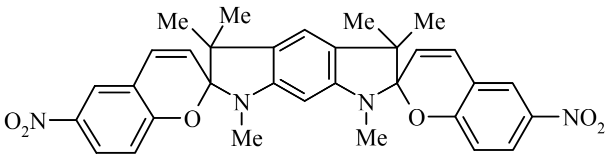


52



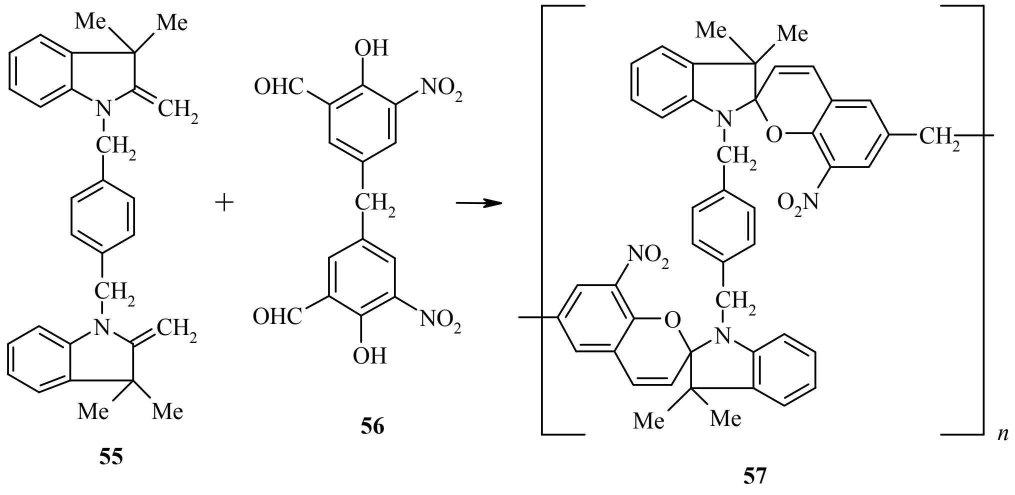
53

A spirobipyran **54**, synthesized from a derivative of hexahydropyrrolo[3,2-*f*]indole, is known. The absorption band of the open form at 598 nm indicates that only one ring is opened [87].

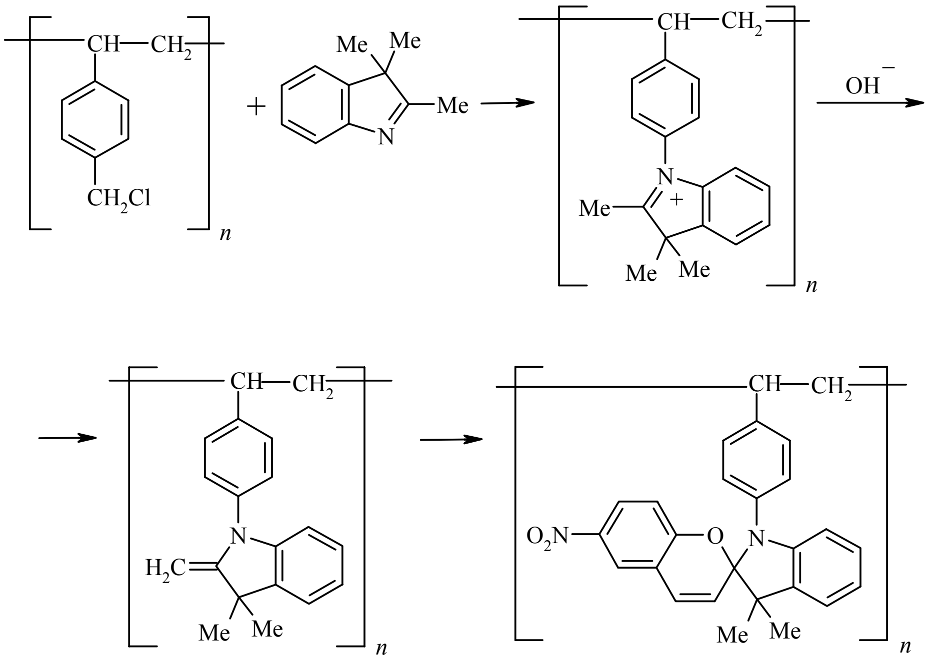


54

The two bifunctional partners bis-2-methyleneindoline **55** and bissalicylaldehyde **56** can undergo polycondensation, leading to the photochromic polymer **57** containing spiropyran units [88].

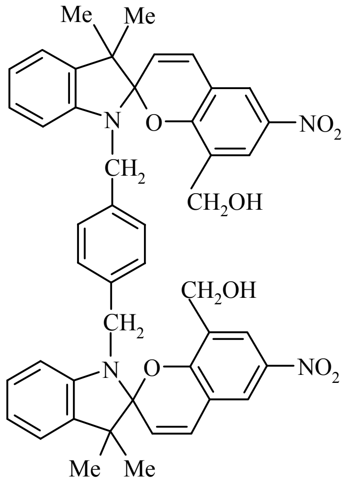


A photochromic polymer **58** containing spiropyran units can be obtained by using a different synthetic principle, i.e., modification of substituents in the polymer chain by means of reactions leading to the formation of a spiropyran structure [89].

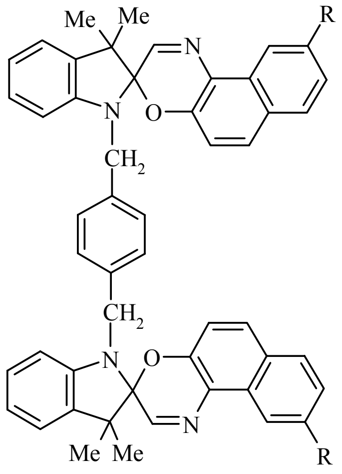


58

With bis-2-methyleneindoline the bisspiropyrans **59** and their hetero analogs the spirooxazines **60** were obtained [90].



59

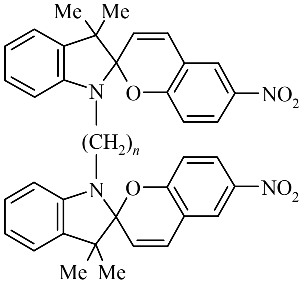


60

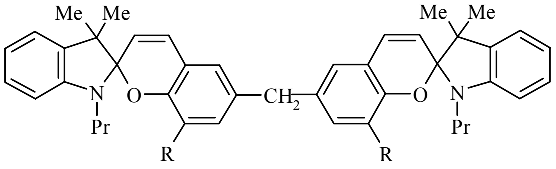
R = H, OMe

Investigations into the photochromic characteristics of the obtained compounds showed insignificant difference between the mono- and bisspiropyrans. The absorption bands of the open forms lie in the region of 580-600 nm, indicating that only one ring is opened.

The bisspiropyrans **61** and **62** were obtained similarly [91].

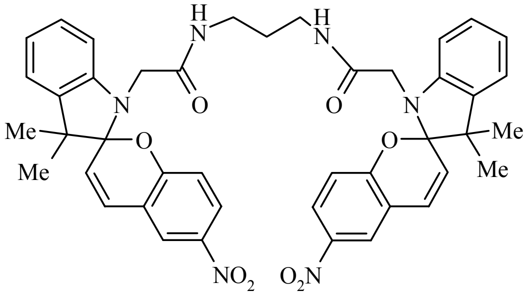


61 $n = 2, 4, 6$



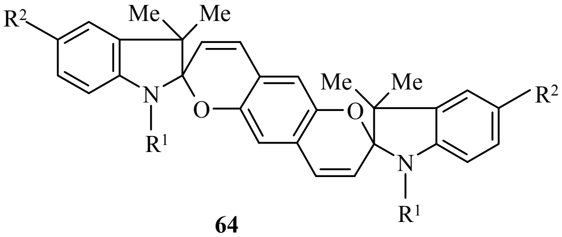
62 R = H, NO_2

The bisspiropyran **63** was obtained by the condensation of a mixture of 2 mole of 1,2,3,3-trimethylindolenylium, 1 mole of 1,3-bischloroacetamidopropane, and 2 mole of sodium iodide with 2 mol of 5-nitrosalicylaldehyde. As stated by the authors in [92], both spirocycles are opened during the formation of complexes with calcium and magnesium.



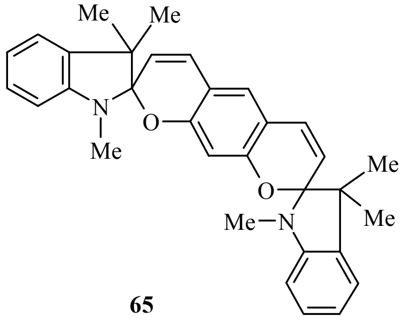
63

Symmetrical indoline bisspiropyrans **64-66** in which the spirocyclic centers are linked to each other through an aromatic system of conjugated bonds are known [86].

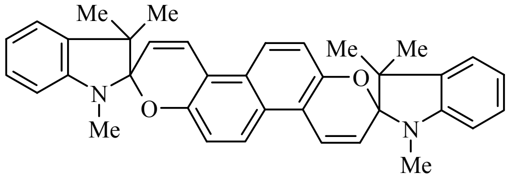


64

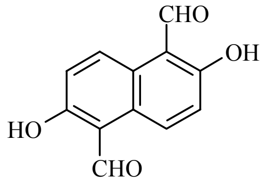
R^1 = Me, Ph; R^2 = H, Cl, Br



65



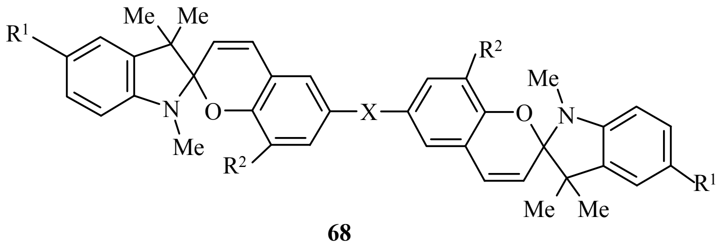
66



67

However, the structure of compounds **64-66** was not confirmed by modern physicochemical methods of analysis, while the initial dialdehyde **67** is subject to doubt in connection with the fact that according to published data [93] it was isolated from the reaction mixture with a small yield only in the form of a hydrazone.

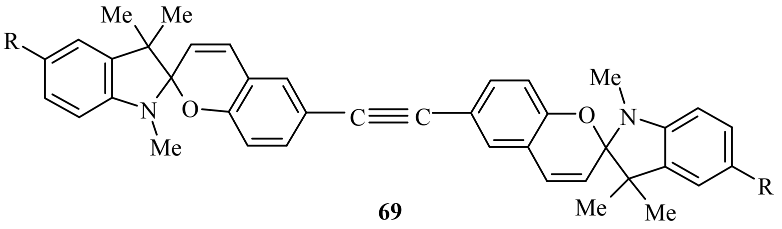
New thermo- and photochromic thia- and carbonylated bisspiropyrans **68** were synthesized by the reaction of 5,5'-thiobissalicylaldehydes or their 5,5'-carbonyl analogs with the derivatives of a Fischer base in a molar ratio of 1:1.25. The thiabisspiropyrans did not exhibit thermo- and photochromism, whereas spiropyrans linked by a carbonyl bridge exhibited weak thermo- and photochromism [94].



68

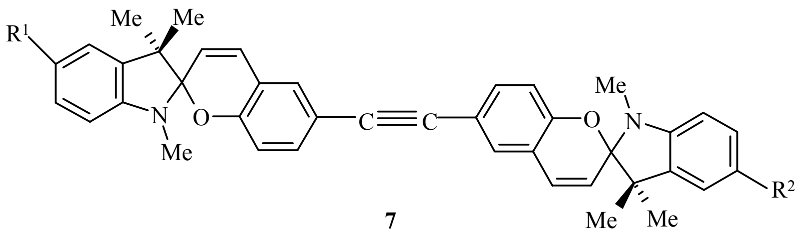
X	R^1	R^2
S	H	H
CO	H	H
CO	H	Cl
S	NO_2	H
S	NO_2	Cl
S	NO_2	NO_2

Symmetrical **69** and unsymmetrical **70** bisspiropyrans linked through a π-bridging unit (acetylene) were also synthesized [95].



69

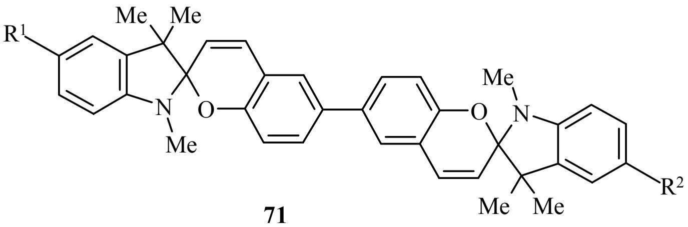
R = H, Cl, PhCONH



7

R^1 = Cl, PhCONH; R^2 = H, PhCONH

Symmetrical and unsymmetrical bisspiropyrans **71** were obtained on the basis of 5,5'-bissalicylaldehyde [96].

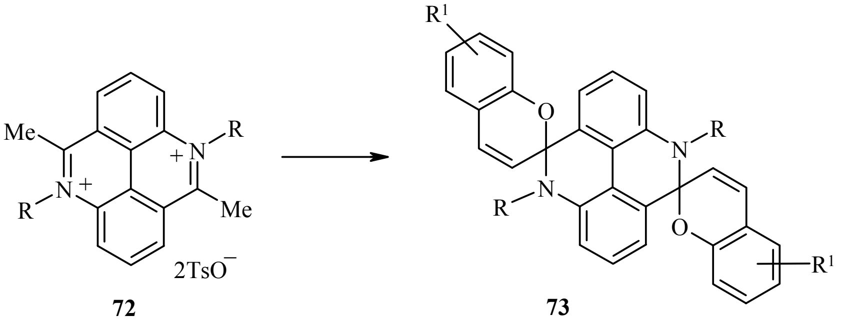


71

R^1	R^2
H	H
H	Cl
H	NHCOMe
Cl	Cl
Cl	NHCOMe
NHCOMe	NHCOMe

It should be noted that in the papers mentioned above [94-96] both unsymmetrical and symmetrical bisspiropyrans were obtained in two stages. The respective bissalicylaldehyde was first condensed with an equimolar amount of 2-methylene-1,3,3-trimethylindoline. At the second stage the isolated monospiropyran reacted with an equimolar amount of the respective 2-methylene-1,3,3-trimethylindoline. This is probably due to the fact that the main condensation products during the direct condensation of bissalicylaldehyde with 2 mol of indoline are compounds of type **8**, the mechanism of formation of which was described in detail in the review [14].

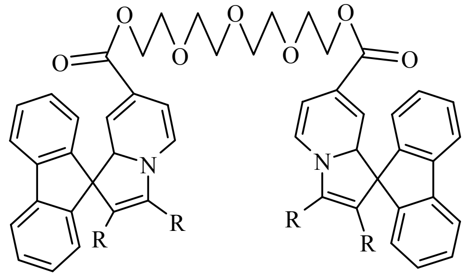
The colorless spiropyrans **73** are formed during the condensation of diquaternary salts of 5,10-dimethyl-4,9-diazapyrene **72** with substituted salicylaldehydes with heat in alcohol or DMF with the addition of piperidine [97].



72 **73**

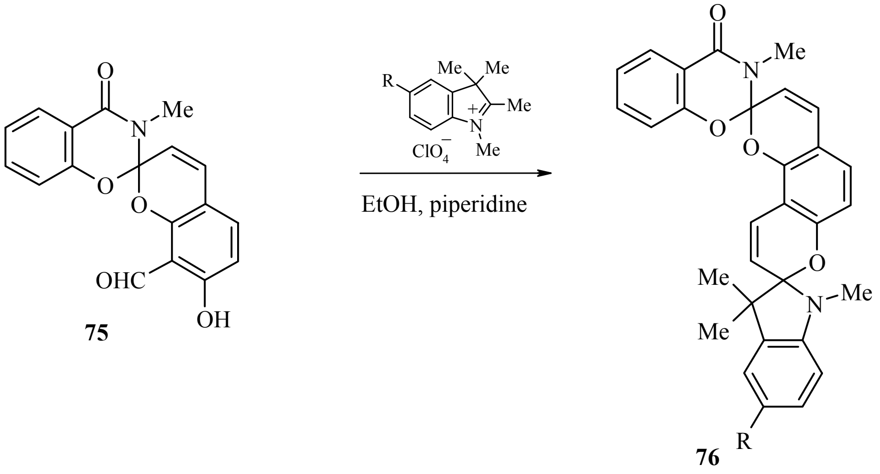
R = Me, Et; R^1 = 6',6''-OMe; 8',8''-OMe, 5',6',5'',6''-dibenzo; 6',6''-Br_2; 6',8',6'',8''-Br_4

There has recently been an active search for various alternative bisspiro compounds having photochromic characteristics. Thus, the bisspiro compound **74** was described in [98].



74

The spiropyran **76** containing two different spirocyclic centers and, accordingly, two different hetarene fragments in the molecule was synthesized on the basis of the obtained spiropyran **75**, which is a unique analog of salicylaldehyde [99].



4. CHEMICAL CHARACTERISTICS OF SPIROPYRANS

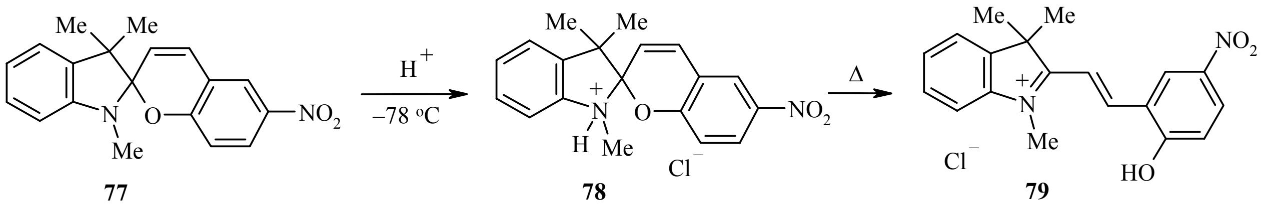
The first and most far-reaching chemical characteristic of spiropyrans, discovered at the beginning of the twentieth century, is the reversible transformation into the colored forms. It can take place during dissolution in polar solvents, during heating (thermochromism [2-4]), or under the influence of activating radiation (photochromism [5]).

The general scheme for such transformations includes the initial formation, during cleavage of the C_{spiro}–O bond, of a [2H]chromene fragment of bipolar form, which can be transformed into a quinoid form with a different configuration for the polymethine chain [15].

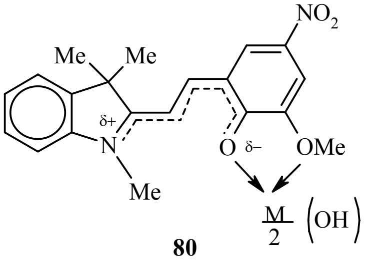
A similar process can also occur during the adsorption of spiropyrans, where the polarizing effect of the adsorbents is significantly stronger than that of the solvents [100-103] right up to destruction of the spiropyran. During the adsorption of 8'-methoxy-6'-nitro-1,3,3-trimethylspiro(indoline-2,2'-[2H]chromene) on silica gel the "initial" 3-methoxy-5-nitrosalicylaldehyde was isolated in an amount that depended on the activity of the silica gel [104].

During the action of acids on solutions of the spiropyrans opening of the [2H]pyran ring may be accompanied by the addition of a proton to the phenolate oxygen atom of the bipolar form [105, 106].

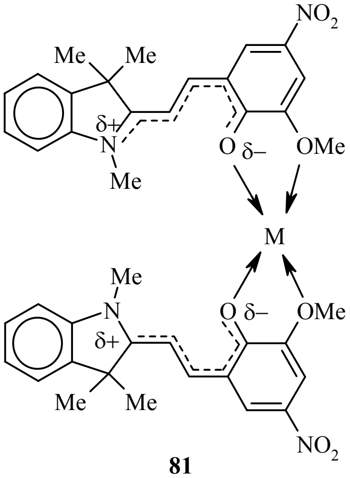
Later on in the case of 6'-nitro-1,3,3-trimethylspiro(indoline-2,2'-[2H]chromene) **77** it was possible to isolate two salts with HCl, differing in physical characteristics. In toluene at -78°C a yellowish salt **78** is formed, and this is converted completely into the isomer **79** during storage or on boiling in alcohol for 10 min [7]:



The action of metal ions during the complexation of spiropyrans of the indoline series was first studied in [107, 108]. It was found that in polar media this process takes place without irradiation and, as believed, with participation of the merocyanine form of the spiropyran. During UV irradiation the yield of the complexes is increased on account of increase in the concentration of the merocyanine form. Investigation of the kinetics of complexation by the stopped-flow method indicates the presence of at least two stages differing substantially in time. The first fast stage takes place with the formation of compound **80**. The second slow stage involves reaction of the complex **80** with the open form of the spiropyran with the formation of the stable complex **81** [109, 110].



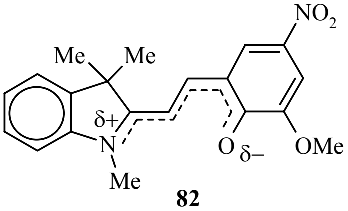
80



81

The complexation of spiropyrans was studied by nanosecond laser photolysis, making it possible to detect the fast stages ($\tau \leq 10^{-3}$ sec) and demonstrating the participation of intermediate *trans* isomers with various stability in the reaction [111]. The ability of the spiropyrans to form complexes with Mn(II), Co(II), Ni(II), Zn(II), and Cu(II) ions with UV irradiation to form the complexes **80** was demonstrated [16].

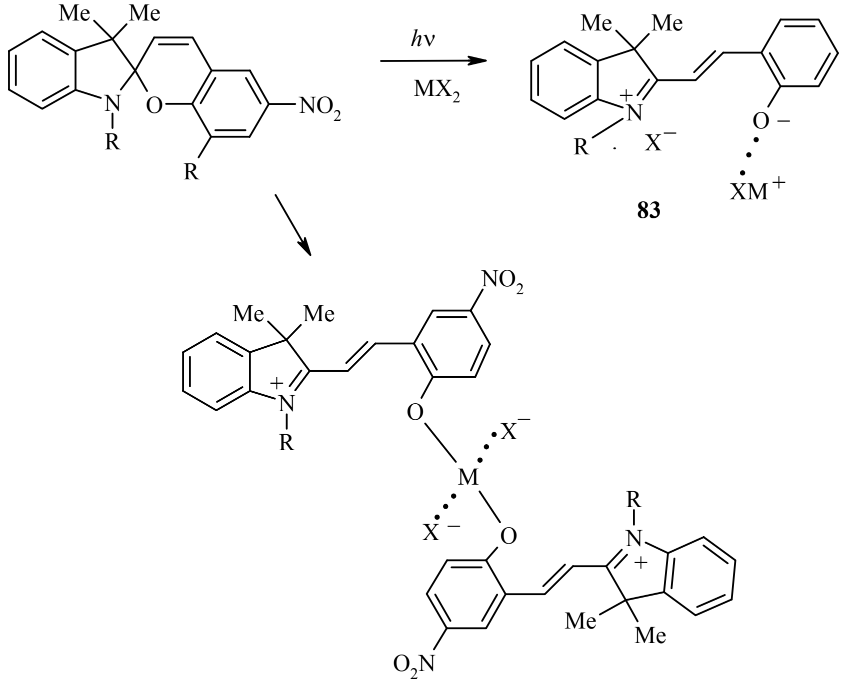
The merocyanine form **82** has weak luminescence on account of rapid deactivation of the excited state, occurring as a result of stereoisomerization.



82

There is a possibility of complex formation between the merocyanine form of the spiropyran and the ions of transition metals without UV irradiation. The reaction is accompanied by spectral changes in the visible region, and this formed the basis of a method for photometric determination of the elements. There are luminescence data for the complexes of spiropyrans with certain transition and rare-earth elements.; complexation with the ions of La, Y, Er, and other rare-earth metals leads to a strong increase in the intensity of luminescence with a simultaneous shift of the luminescence maximum toward short wave lengths [112]. Thus, the open merocyanine form of spiropyran forms metal complexes having characteristic absorption spectra and is of interest for the development of methods for the determination of metals based on color reactions.

There are a series of metal complexes of type **83** and **84** that extend the life time of the merocyanine form of spiropyrans [113-116].

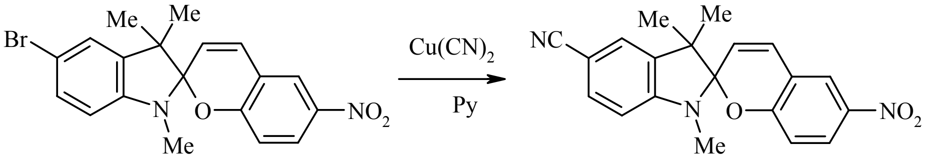


83

84

Complexes of bisspiropyrans are known, and their complexing ability has been studied in comparison with monospiropyran [99, 117, 118]. It was found that the complexes of bisspiropyrans have higher photochemical activity than those of monospiropyrans.

The cyclic forms of spiropyrans enter readily into various substitution reactions. Thus, for example, during bromination of 1,3,3-trimethylspiro(indoline-2,2'-chromene) with bromosuccinimide in chloroform the bromine enters at position 5 of the indoline fragment, while the action of an excess of bromosuccinimide leads to the formation of the 5,7,3',6'-tetrabromo derivative [119]. The use of the halides of divalent copper in the presence of aluminum chloride or complexes of boron trifluoride as halogenating agents leads to the formation of the 5-halo derivatives [120]. During the action of bromine in chloroform on 5,6'-dinitro-1,3,3-trimethylspiro(indoline-2,2'-chromene) the bromine atom enters at position 7 of the indoline fragment with the formation of 7-bromo-5,6'-dinitro-1,3,3-trimethylspiro(indoline-2,2'-chromene). There is also interest in the possibility of replacing the bromine atom at position 5 of the indoline fragment by a cyano group [121]:

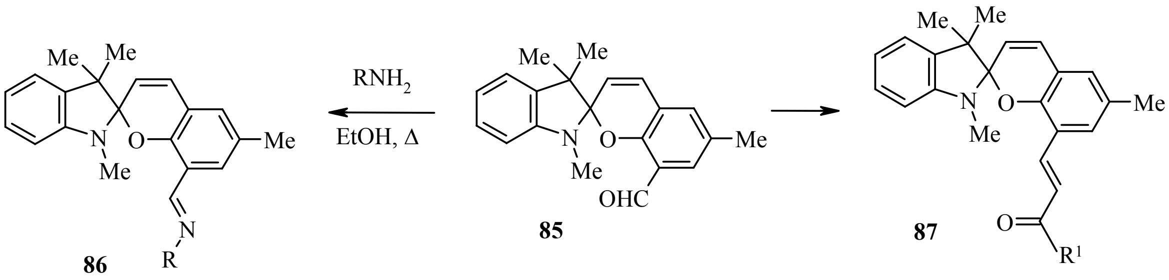


During the action of nitric acid in acetic anhydride on 6'-nitro-1,3,3-trimethylspiro(indoline-2,2'-chromene) the nitro group enters at position 5 of the indoline fragment. It can then be reduced by molecular hydrogen at a platinum electrode to an amino group, which is readily acylated by the acetic anhydride [118].

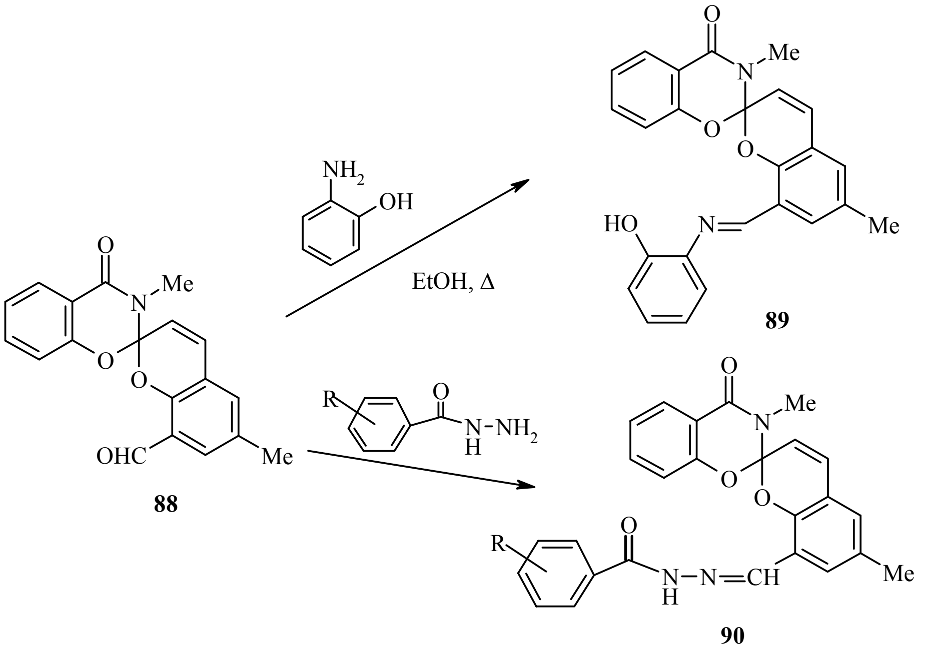
By the action of sodium nitrite on indolinospiropyrans in acetic acid it is possible to introduce a nitroso group at position 5 of the indoline fragment. During oxidation by atmospheric oxygen it forms a nitro derivative [120]. Azo coupling of phenyldiazonium salts with indolinospiropyrans takes place at position 5 of the indoline fragment, which is marked by high reactivity. Acylation with acetic anhydride in the presence of complexes of boron trifluoride or benzoyl chloride in dimethylaniline leads to entry of the acyl group at position 3' [122].

Acylation of the hydroxy group in N-(β-hydroxyethyl) derivatives of indolinospiropyrans [123-125] and thiazolinospiropyrans [126] is also possible, although this reaction is accompanied by the formation of side products.

Extension of the possibilities of synthesizing new spiropyrans using the functional possibilities of the substituents in the spiropyran structures was demonstrated for the case of derivatives of indolinospiropyrans **85**, containing a free formyl group. Their reaction with amines gave the azomethines **86**, while condensation with methyl (aryl) aryl ketones gave the corresponding ketovinyl derivatives **87** [29, 127].

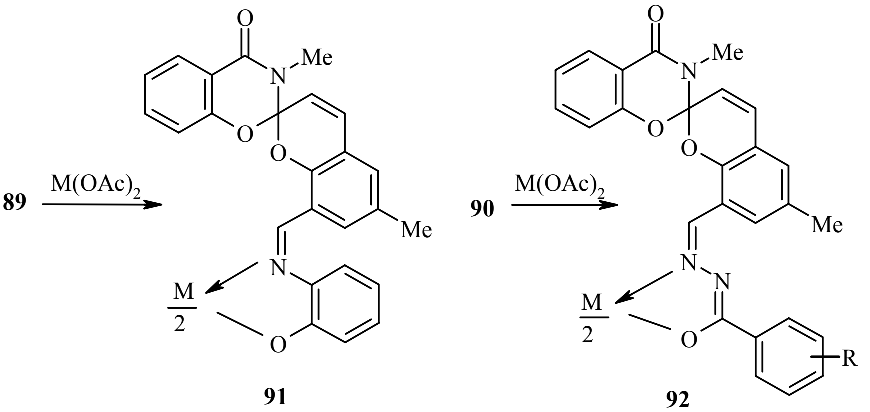


New spiropyrans of the benzoxazinone series **89** and **90** were obtained similarly from 3,6'-dimethyl-8'-formylspiro(4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2,2'-[2H]chromene) **88**, which exhibits photochromic characteristics in the solid phase [26]. It was shown that the identification of spiropyrans containing π-accepting hydrazone substituents must be conducted at elevated temperatures with tracking of the presence and completeness of subsequent "recovery" during cooling to 30°C. According to X-ray crystallographic analysis, crystal solvates of the target compounds can be formed, depending on the solvent used for recrystallization of the hydrazones containing the spiro carbon atom [128].



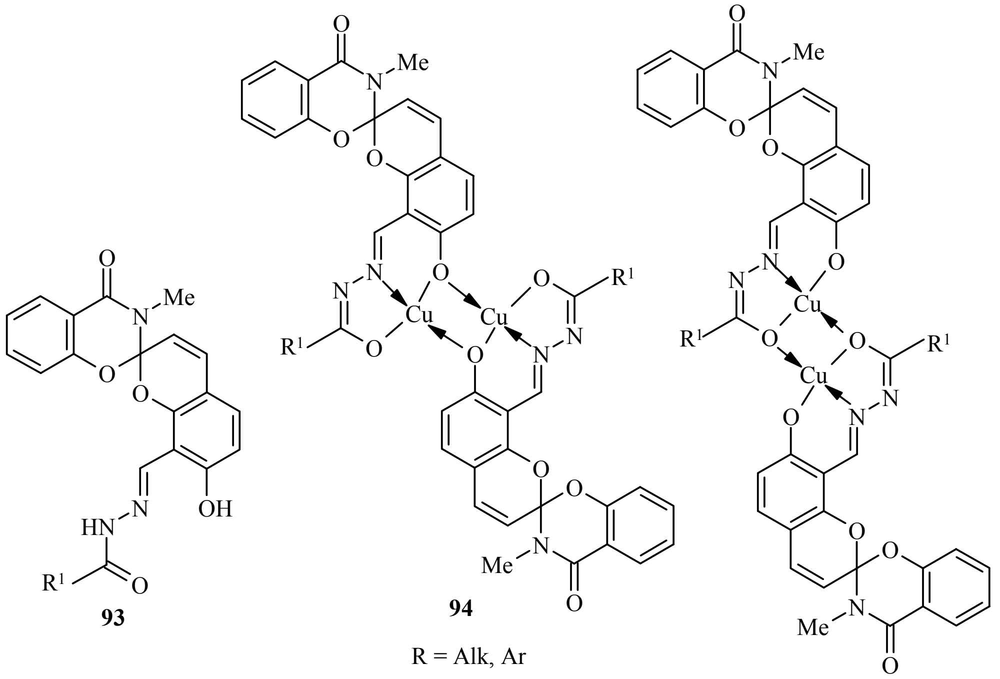
Metal chelates **91** and **92** were obtained on the basis of the imines **89** and hydrazones **90**, containing a spiropyran fragment of the 3-methyl-4-oxo[2H]-1,3-benzoxazinone series. The possibility of an effect from nontraditional π-accepting substituents [the products from condensation of the formyl group of 3,6'-dimethyl-8'-

formylspiro(4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2,2'-[2H]chromene) with *o*-aminophenol and the hydrazides of aromatic acids] and the complexes of the ions of transition metals was investigated [129].



91 **92**

The hydrazones **93**, used as ligands for the synthesis of binuclear complexes of copper **94** and **95** [130], were obtained on the basis of the spiropyran **75**, which contains *ortho*-located hydroxy and formyl groups in the benzene ring of the [2H]chromene fragment [99].



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R = Alk, Ar

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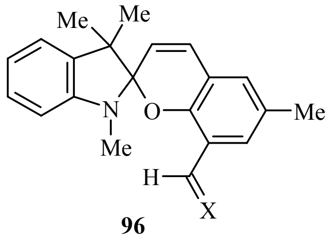
5. PHOTOCHROMIC CHARACTERISTICS OF SPIROPYRANS

Spiropyrans are the most widespread class of organic photochromes, the proposed mechanism [131] of photocoloration of which has not been finally established. Nevertheless, it was shown on the basis of analysis of the structure and the photochromic characteristics of indoline spiropyrans that their photochromic characteristics, due to electrocyclic cleavage of the C_{spiro}–O bond with photoexcitation, are largely predetermined already by the fact that in the ground state this bond is elongated and weakened on account of orbital interactions between the unshared electron pair of the indoline nitrogen and the antibonding orbital of the C_{spiro}–O bond [132-134]. The C_{spiro}–S bond is also elongated in spirothiapyrans, but this is due not to specific orbital interaction but to the steric strain of the molecule [135].

Of particular interest for a number of utilitarian purposes are spiropyrans in which the long-wave maximum of the absorption band of the photoinduced form has maximum shift toward the long-wave region of the spectrum.

Theoretical investigations of the effect of substituents on the spectral characteristics of the photoinduced forms made it possible to find a range of compounds with a strong bathochromic shift of the long-wave band in the open-chain isomer. This is achieved primarily by the introduction π-accepting substituents such as, for example, the nitro group into the benzene ring of the chromene part of the spiropyrans [10, 16].

In the case of indoline spiropyrans **96** it was shown that the introduction of π-accepting substituents other than nitro groups into the molecule gives a significant bathochromic shift of the absorption band of the photoinduced form [29, 136].



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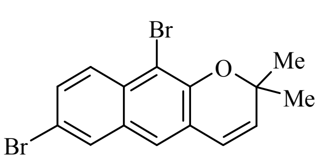
X = O, CHCOAlk; CHCOAr, *p*-$CHC_6H_4NO_2$

A significant bathochromic shift of the long-wave absorption band of the photoinduced forms of spiropyrans is also achieved by replacing the oxygen by sulfur in the pyran fragment of the molecule; the λ_{max} values of the colored forms of 6'-nitro-1,3,3-trimethylindolinospiropyran and 6'-nitro-1,3,3-trimethylindolinospirothiapyran are 532 [7] and 680 nm [81] respectively.

A special case is presented by spiropyrans with linearly annelated rings (6,7-benzannelation in the chromene part). As shown by quantum-chemical calculations, in such systems the long-wave maximum of the absorption band of the photoinduced form [69] should be observed in the region of 750 nm. However, for such a spiropyran of the 2-oxazolidone series the most long-wave absorption band in the spectrum of the photoinduced form is observed experimentally at 461 nm [61], and for spiropyran of the 2-thioxooxazolidinone series it is observed at 480 nm [62]. Since the photochromic characteristics of the spiropyrans are due to opening of the benzopyran ring, the model [2H]chromene **97** was synthesized in order to exclude the supposed effect of the hetarene fragment on the spectrum of the colored form [61]. However, the long-wave absorption band of its photoinduced form is observed at 425 nm, which also disagrees with the calculated wavelength (539 nm) [137].



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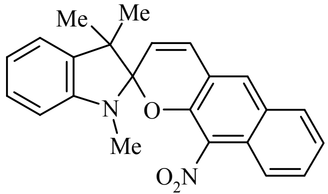
However, it was shown during study of the photochromic characteristics of the spiropyran **98** [138] that together with the absorption band at 460-465 nm a long-wave maximum also appears in the form of a diffuse absorption band in the region of 500-700 nm.



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The photochromic characteristics of spiropyrans have been studied quite well both in solutions and in polymeric matrices [7, 17], but a systemic study of their photochromic characteristics at the phase boundary has not so far been undertaken. Among the spiropyrans "solid-phase" photochromes of the indoline series, containing nitro and methoxy groups simultaneously, are known, e.g., 5'-bromo-8'-methoxy-6'-nitro-1,3,3-trimethylspiro(indoline-2,2'-[2H]chromene) and 5'-bromo-8'-methoxy-6'-nitro-1,3,3-trimethyl-7-phenylspiro-(indoline-2,2'-[2H]chromene). To produce photochromic materials based on them the glass substrates are treated with a solution of a mixture of spiropyrans with the essential retention of the obtained amorphous layer during drying, since with its possible crystallization the photochromic characteristics disappear [139]. Another example 1-allyl-3,3-dimethyl-6'-nitrospiro(indoline-2,2'-[2H]chromene) exhibits photochromic activity in crystals but has low sensitivity, while 1,3,3-trimethylspiro(indoline-2,2'-[2H]chromene) exhibits photochromic characteristics at 0°C in the glassy film produced when the molten spiropyran is cooled [13]. During spectrofluorimetric study of monolayers of 3,3-dimethyl-6'-nitro-1-octadecylspiro(indoline-2,2'-[2H]benzopyrans) a change in surface tension was detected at the water–air interface together with the photochromic characteristics [140]. Monolayers of 1-hexadecyl-3,3-dimethylspiro(indoline-2,2'-[2H]benzopyran) and its (3H)naphtho[2,1-*b*] derivative adsorbed on quartz possess direct photochromism and are decolorized by the action of visible light [141]. The photochromic characteristics are preserved in some indolinospiropyrans adsorbed on the surface of aluminum and silicon oxides and also on the surface of certain aluminosilicates, but the photochromic process is characterized by unusually high reversibility compared with neutral solutions as a result of complexation between the spiropyrans and the surface of the oxides [142]. The behavior of photochromic indolinospiropyrans adsorbed on a membrane of 2,4-diacetylcellulose was studied. It was shown that exposure of such a membrane leads to a change in the membrane potential, due to a change of the density of charge on the membrane as a result of the transition from the closed form of the spiropyran to the open merocyanine form [143]. The colorization of oriented films of indoline spiropyrans (produced by evaporation of the solvent from glassy substrates) is accompanied by an increase in their thickness and is due to change in the size of the molecule during ring opening [144]. The low effectiveness of photocolorization in the N-methyl derivatives compared with the compounds containing long N-alkyl chains (6, 7, 8, 12, and 18 carbon atoms) is due to the greater mobility of the latter, which facilitates isomerization of the colored merocyanine form to the colorless cyclic form [145].

1,3,3-Trimethyl-8'-formylspiro(indoline-2,2'-[2H]chromene) exhibits photochromic characteristics during adsorption on paper dried after impregnation with a solution of spiropyran in benzene or toluene. After exposure of the obtained material in UV light a blue image is obtained [146]. The action of light with λ_{max} < 360 nm on a film produced by vacuum deposition of 6'-hydroxy-1,3,3-trimethylspiro(indoline-2,2'-[2H]benzopyran) leads to its colorization. However, the reverse process under the influence of visible light or heat does not go to completion since the film after deposition is in a nonequilibrium state. The equilibrium established in the course of photolysis or heating is accompanied by the partial formation of the merocyanine form, stabilized by interaction with the acidic phenolic groups [147].

In the thin films of 1',3',3'-trimethylspiro[2H-1-(phenyl-3-isopropylpyrazolo)[4,5-*e*]thia(selena)pyran-2,2'-indolines] exhibiting photochromic characteristics in the solid phase, produced as a result of vacuum thermal deposition, the long-wave absorption band of the photoinduced form of the selenapyran derivative undergoes a bathochromic shift in relation to its thia analog [73].

Spiropyrans of the indoline [137] and benzoxazinone [27, 148] series, containing a formyl group at position 8', exhibit photochromic activity in the solid phase, i.e., in thin polydisperse films produced as a result of vacuum thermal deposition ($P = 10^{-5}$ torr, evaporation temperature 450-500°C) of the targeted compounds onto transparent substrates. Such films have reversible photochromic characteristics. The broad absorption band of the colored form makes it possible to read written data by means of a helium–neon laser [λ = 632.8 nm (~15803 cm^{-1})] and to write data by means of a nitrogen laser [λ = 337 nm (~29674 cm^{-1})] [136].

During investigation of the enantiomerization of indoline spiropyrans containing a free formyl group at position 8' of the benzopyran fragment and capable of exhibiting photochromic characteristics in the solid phase a tendency for the free energy of activation (ΔH_{298}) of ring opening to increase was detected [149].

The recently obtained [99] spiropyran of the indoline series containing *ortho*-located formyl and hydroxy groups in the benzene ring of the [2H]chromene fragment exhibits photochromic characteristics in the adsorbed state and contains centers capable of chelation with a metal. The length of the hydrogen bond, determined from X-ray crystallographic analysis, amounts to 1.978 Å [150].

The data from X-ray crystallographic analysis were also used to refine the structural factors determining the photochromic activity in the solid phase of spiropyrans of the benzoxazinone series [26, 151].

Spiropyrans of the oxaindane and indoline series that exhibit photochromic characteristics during adsorption on the surface of films of silver were studied by giant Raman spectroscopy [152-154].

6. APPLICATION OF SPIROPYRANS

Photochromic compounds based on spiropyrans, spirooxazines, and [2H]chromenes are prospective silver-free light-sensitive materials for the optical recording of data, the creation of photoswitches, light filters with modulated transmission, and miniature hybrid multifunctional materials.

The conceptual aspects of the practical application of spiropyrans in various regions of technology, connected primarily with the photo-, thermo-, solvato-, and electrochromic characteristics [155], were formulated in the monograph [10] and the text book [9] and were supplemented by the review [12].

Spiropyrans of the traditional indoline [156] and other series based on nitrogen-containing heterocycles [157] and also indolinospirothiapyrans, which are characterized by a shift of the absorption band of the photoinduced form toward the red region of the spectrum [79-81], have found application. Polyester resins have traditionally been used to produce film forms of photochromic materials based on spiropyrans [158, 159]. Photochromic materials from spiran-containing polymeric films deposited on a paper base have become widespread [156, 159]. Synthetic resins with a high refractive index were used to make photochromic lenses [160]. Spiropyrans have even found their uses in cosmetic compositions [161].

The creation of modern photochromic materials [162, 163] requires a combination of new types of spiropyrans [164] with modified supports and in particular Langmuir–Blodgett films containing spiropyran as photoreceptors [165], and also films containing rhodopsin to increase the level of the photosignal [166]. Photochromic materials based on spiropyrans sensitive to UV radiation [167] have traditionally been used as detectors [168], for the protection of sight organs [169], for the creation of light filters with modulated transmission and devices based on them [170], and photochromic lenses [171], including ophthalmic lenses [172].

The use of compositions based on spiropyrans for the creation of materials for recording optical data [173, 174] in various devices [175], including thin films [176], was supplemented by the creation of novel media sensitive to IR radiation [177, 178]. This made it possible to use semiconductor lasers as activating source of radiation [179].

Powdered and film materials based on ion-containing complexes of spiropyrans [181] and also spiropyran copolymers [182] have also been used to record optical data [180] and increase the duration of its storage.

Carboxylated spiropyrans have been used for determination of the activity of peroxidase [183] and in systems for the determination of low-level NO_2 content in the environment [184].

Spiropyran finds widespread use as molecular logic devices [185], including for the production of nanostructured photochromic films from biopolymers [186], photochromic and electrooptical devices [187], molecular and supramolecular logic switches [188], photoswitches [189], and multifunctional artificial receptors [190].

Photochromic spiropyrans are promising for use in the creation of various types of optical memory [191] in quantum computers [192].

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