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Spirooxazines: synthesis, structure, spectral and photochromic properties

V Lokshin, A Samat, A V Metelitsa

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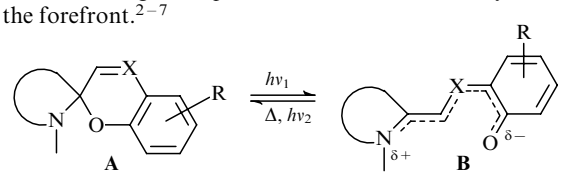
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Abstract. The review surveys synthetic approaches to spiro[1,4]oxazines belonging to one of the most promising classes of organic photochromes. The relationships between the structures of spirooxazines and their spectral properties as well as characteristics of thermal and photoinduced processes are considered. The bibliography includes 201 references.

I. Introduction

Reversible molecular rearrangements are of great interest because they play an important role in studies of many chemical and biological processes, which find use in modern technologies. Of special interest are light-induced rearrangements, the so-called photochromic rearrangements. These are reversible transformations of a chemical species between two states with different absorption spectra induced (at least in one direction) by electromagnetic radiation.[1] In recent years, photochromic organic compounds have been extensively studied because of their application in optical systems for recording and retrieval of information, molecular switches, dynamical chemosensors and biosensors, systems for accumulation of solar energy, transport systems, catalysis, optoelectronics and optobioelectronics.[1–7] Since organic photochromic compounds find application in diverse fields, requirements on their characteristics are rather wide. In this connection, the directed synthesis of these compounds assumes great importance. Directed syntheses are planned taking into account the results of investigations on general relationships between the molecular structure and spectral-kinetic properties of photochromic compounds.

Photochromism was first described at the end of the 19th century. However, extensive studies of organic photochromes were started only in the second half of the 20th century. Spirocyclic compounds composed of two heterocyclic fragments, which are linked through the sp^3-carbon atom, immediately have come to the forefront.[2–7]

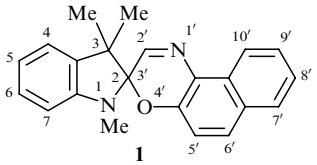


X = CH (spiropyran, SPP), N (spirooxazine, SPO).

The spirocyclic form **A** of these compounds has absorption in the UV region. Excitation of this form with light of the corresponding wavelength causes the cleavage of the $C_{sp^3}-O$ bond followed by isomerisation to give the flattened conjugated form **B**, which has absorption in the visible region.

Of the two above-mentioned classes of spiro compounds, spiropyrans were the first to be synthesised. In the 1960 – 70s, spiropyrans were the best studied organic photochromes.[2] On the background of these extensive studies, the synthesis of the first spirooxazines in 1961 [8] as well as two subsequent publications dealing with these compounds [9,10] went unnoticed.

The starting point for the studies of the chemistry of SPO were investigations by Chu.[11–13] In the beginning of the 1980s, he was the first to discover the extraordinary high photostability† of spiro{indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine} (**1**) and its derivatives under continuous irradiation.



1

† Hereinafter, the photostability is taken to mean the resistance to photodegradation.

V Lokshin, A Samat University of the Mediterranean, Faculty of Science of Luminy, Box 901, F-13288 Marseilles Cedex 9, France.
Fax (33-491) 82 93 01. Tel. (33-491) 82 94 08.
E-mail: lokshin@luminy.univ-mrs.fr (V Lokshin).
Tel. (33 491) 82 94 05. E-mail: samat@luminy.univ-mrs.fr (A Samat)
A V Metelitsa Research Institute of Physical and Organic Chemistry, Rostov State University, prosp. Stachki 194/2, 344090 Rostov-on-Don, Russian Federation. Fax (7-863) 243 46 67. Tel.(7-863) 243 34 00.
E-mail: met@ipoc.rsu.ru

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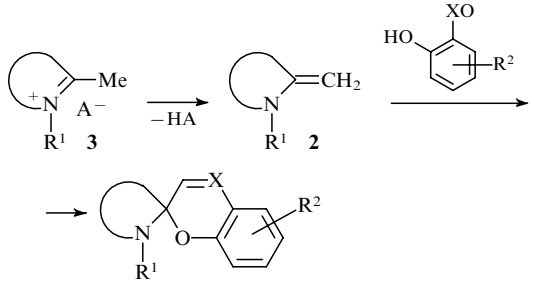
Due to this discovery, SPO have attracted the attention of researchers as photochromes showing promise for the practical use in materials with varying optical density. Since the mid-1980s, the number of publications (especially patents) devoted to SPO sharply increased, which gave impetus to their systematisation and analysis.

Spirooxazines were the subject of three reviews,[4,6,14] two of which were chapters of monographs. Unfortunately, problems of the synthesis and structural modifications of SPO remained virtually beyond the scope of the reviews[4,6] and received proper attention only from Japan researchers.[14] However, the latter review was published more than a decade ago. In recent years, abundant new data on the synthesis of SPO have become available. Taking into account an importance of synthetic aspects, which, to a great extent, determine new areas of practical application of SPO, we believe that there is a need to consider these problems in more detail, with emphasis on the results obtained in the last 10–12 years. In citing patent data, we take into account only studies (with rare exception), which gave clear characteristics of the compounds (melting points and/or informative NMR spectra). The effects of the structural factors on the spectral properties and characteristics of thermal and photoinduced processes of spirooxazines in solutions are considered. For a correct comparison, prominence is given to the results obtained in approximately identical conditions.

II. Synthesis of spirooxazines from aromatic *o*-hydroxynitroso compounds

1. Conditions and reaction mechanism

One of the most commonly used procedures for the synthesis of SPO from aromatic *o*-hydroxynitroso compounds and alkylidene derivatives of nitrogen-containing heterocycles **2** (hereinafter, the 'nitroso' method) was borrowed directly from the chemistry of SPP with the only difference that the reactions with alkylidene derivatives **2** were carried out with aromatic *o*-hydroxynitroso compounds instead of aldehydes, such as salicylaldehyde.



X = CH (SPP), N (SPO).

Alkylidene derivatives **2** are generally prepared *in situ* by the reactions of bases (most often, triethylamine) with the corresponding quaternary salts **3**. Ethanol[9,10] or methanol[13] are traditionally used as solvents, although trichloroethylene,[15–17] toluene,[18,19] dioxane,[20] acetone,[21] chloroform,[22] amyl alcohol[23] and a heptane–ethanol mixture[24,25] have also found use in recent years.

Unfortunately, as have been mentioned in the review by Chu,[4] this method affords SPO in low yields (on the average, 30%–50%). The main reasons for low yields are as follows:

— low reactivity of the nitroso group due to the low electrophilicity of the nitrogen atom;

— instability of some SPO and nitroso compounds in the reaction conditions;

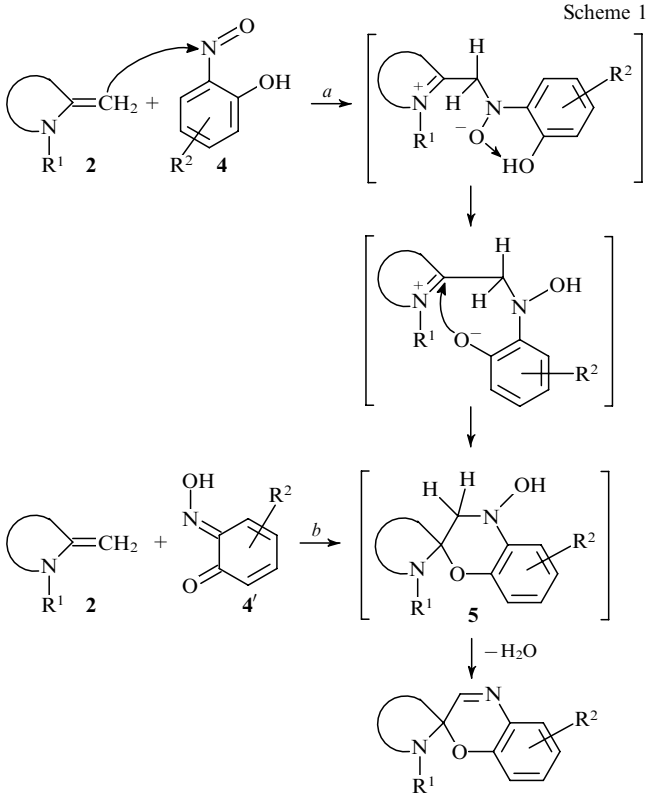
— difficulties associated with the chromatographic isolation of SPO (close values of R_f of SPO, starting compounds and by-products).

A number of recent studies were aimed at optimising the yields of SPO in these reactions. Thus, it has been found[26] that the presence of a drying agent and elevated pressure have a positive effect on the yield of SPO **1** (determined by liquid chromatography). An excess of nitrosonaphthol and the use of toluene as the solvent have the same effect (however, this hinders the isolation of the final product).

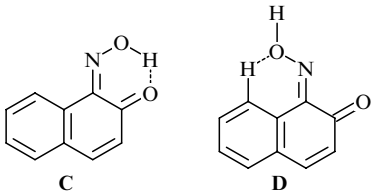
Recently, it has been demonstrated‡ that the reactions performed in the absence of a solvent under microwave activation led not only to a noticeable increase in the yield of SPO but also to an essential decrease in the reaction time (up to ~ 15 min) and reduction in the amount of impurities. This procedure for the synthesis of spirooxazines deserves further investigation.

The mechanism of the reactions of aromatic *o*-hydroxynitroso compounds **4** with alkylidene derivatives of nitrogen-containing heterocycles **2** remains virtually unknown. It was assumed that this mechanism is analogous to that of the synthesis of SPP[27] and involves the attack of the negatively charged carbon atom of enamine on the nitrogen atom of the nitroso group as the first step (Scheme 1, path *a*).

Scheme 1



However, another point of view was expressed in the study.[28] The authors of the cited study believed that the key step involves the electrocyclic reaction of enamine **2** with the quinone oxime tautomer of *o*-hydroxynitroso compound **4′** giving rise to intermediate **5** (Scheme 1, path *b*). This mechanism is indirectly supported by the fact that the quinone oxime forms are much more stable in solutions than the nitrosophenol forms. For example, the NMR spectroscopic study of 1-nitroso-2-naphthol in such solvents as $CDCl_3$, C_6D_6, DMSO-d_6 and dioxane-d_8 revealed the presence of two isomers of the quinone oxime type (**C**



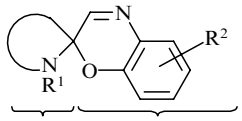
C **D**

‡ A Samat, V Lokshin, R Guglielmetti, J Hamelin, F Texier-Boullet, A V Koshkin, O A Fedorova, S P Gromov *Synth. Commun.* (in preparation).

and **D**), the ratio between these isomers being dependent on the nature of the solvent.[29]

2. Modification of the heterocyclic fragment of spirooxazines

Hereinafter, two fragments involved in the SPO molecule will be referred to as the heterocyclic and oxazine fragments.



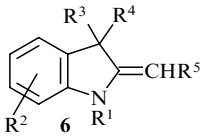
Heterocyclic fragment — Oxazine fragment

Although these names are not strict (oxazine fragment is also heterocyclic), they are, in our opinion, better than such terms as 'left' and 'right' heterocycles, which are sometimes used.

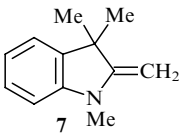
a. Substitution in the indoline ring

The majority of the known spirooxazines involve the indoline ring as the heterocyclic fragment. This preference of researchers is attributable to both the historical tradition associated with the chemistry of SPP and the fact that the replacement of this fragment in SPO by other fragments presents a very difficult problem (see below).

In the synthesis of indoline-containing SPP and SPO, 2-alkylidene derivatives of indoline **6** are used as the starting compounds, of which 2-methylidene-1,3,3-trimethylindoline (**7**) (Fischer's base) is the most well-known representative.



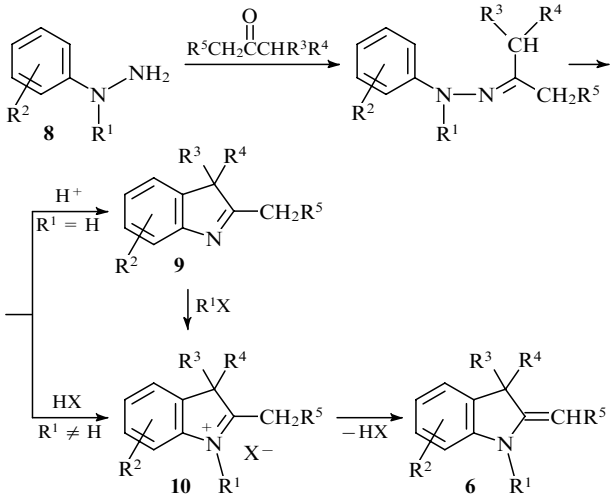
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7

Procedures for the synthesis of these compounds have been developed in considerable detail and have been comprehensively surveyed in reviews.[2, 5, 30] Hence, we will not discuss these procedures in the present review. Let us only note that most of 2-alkylideneindolines were prepared according to the Fischer synthesis (Scheme 2).

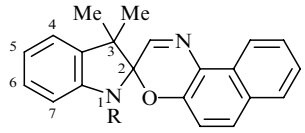
Scheme 2



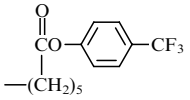
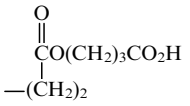
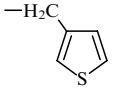
If the starting phenylhydrazine **8** contains hydrogen as the substituent R^1, the reaction affords indolenine **9**. Subsequent alkylation of compound **9** yields quaternary salt **10**, which is converted into 2-alkylideneindoline **6**. In the case that the substituent R^1 cannot be introduced by alkylation, it is inserted into the starting phenylhydrazine **8**.

The Fischer synthesis of indoline-containing synthons is a rather simple process, which accounts for the fact that the substitution in the indoline fragment is most commonly used for the modification of SPO. A substituent is most often inserted at position 1 (at the nitrogen atom) as well as at position 5. Examples of selected 1- and 5-substituted spironaphthooxazines **11**–**32** are given in Tables 1 and 2.

Table 1. 1-Substituted spironaphthooxazines of the indoline series.

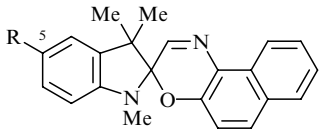


11–**24**

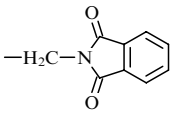
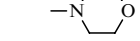
SPO	R	Ref.	SPO	R	Ref.
11	$-(CH_2)_{17}Me$	31 [a]	**18**	$-(CH_2)_2CO_2H$	9, 36
12	$-CH_2Bu^t$	32	**19**	$-(CH_2)_5CH(CO_2Et)_2$	31
13		33	**20**		37
14	$-CH_2CH(Me)Ph$	32	**21**		38
15	$-(CH_2)_2OMe$	34	**22**	$-(CH_2)_5CONH_2$	39
16	$-CH_2Ar$	35	**23**		21
17	$-CH_2CH=CH_2$	26, 31	**24**		40

[a] A series of other *N*-alkyl-substituted SPO were described in the study. [31]

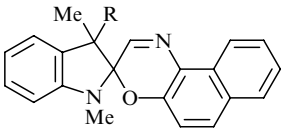
Table 2. 5-Substituted spironaphthooxazines of the indoline series.



25–**32**

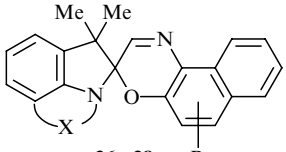
SPO	R	Ref.	SPO	R	Ref.
25	$-F$	41	**29**	$-NO_2$	26
26	$-I$	41	**30**	$-NH_2$	43
27		15	**31**	$-NHCOMe$	15
28	$-OH$	42	**32**		44

3-Substituted derivatives **33**–**35** (see Ref. 44) and unique bridging structures **36**–**38** (see Ref. 45) were synthesised.



33–**35**

R = Pr^i (**33**), CH_2Ph (**34**), Ph (**35**).



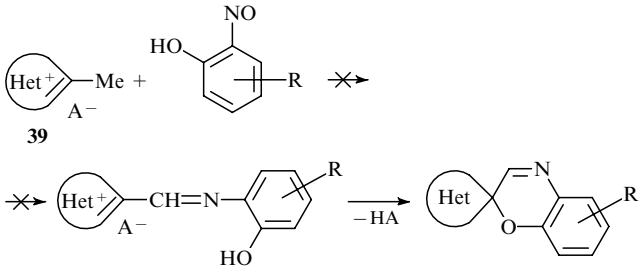
36–**38**

X = $-(CH_2)_3-$ (**36**), $-CH_2C(Me)H-$ (**37**), $-(CH_2)_2C(Me)H-$ (**38**).

It should be noted that substituents in the indoline fragment (particularly, at position 1) not only have an effect on the photochromic properties of SPO but also improve such important useful characteristics of SPO as solubility, affinity for polymeric matrices and photostability.

b. Spirooxazines with non-indoline heterocyclic fragments

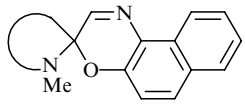
From a synthetic standpoint, the variation in the nature of the heterocyclic fragments in SPO is among the most stubborn problems. Unlike aldehydes of the salicylaldehyde type, aromatic *o*-hydroxynitroso compounds are not involved in condensation with heterocyclic salts of type **39**, except for salts **3**, which give stable bases **2**.



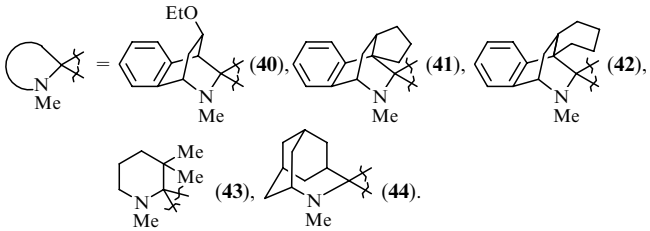
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This fact practically precludes the use of a broad spectrum of oxygen- and sulfur-containing heterocycles, which are successfully employed in the synthesis of SPP.[2] As a result, the range of heterocyclic systems suitable for the synthesis of SPO is limited to nitrogen-containing heterocycles.

New SPO in which the indoline fragment is substituted by sterically hindered (**40**–**42**)[46–49] or saturated (**43**,[50,51] **44**[17,52,53]) azaheterocycles have been synthesised in recent years.

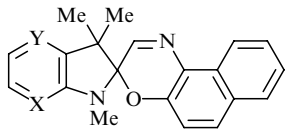


40–**44**



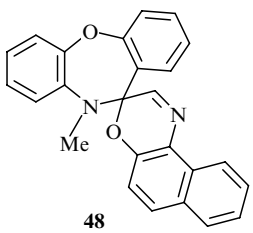
(**40**), (**41**), (**42**), (**43**), (**44**).

Besides, compounds containing azaindoline (**45**–**47**)[20,54] or dibenzooxazepine (**48**)[18,55–57] fragments were synthesised. It should be noted that compound **48** exhibits photochromic properties only at low temperatures (from −40 to −20 °C).



45–**47**

45: X = N, Y = CH;
46: X = CH, Y = N;
47: X = Y = N.

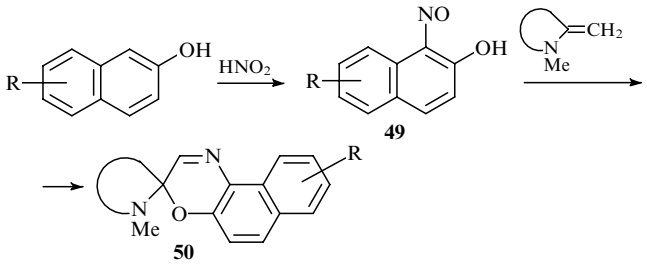


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3. Modification of the oxazine fragment of spirooxazines

a. Substitution in the naphtho[2,1-*b*]oxazine fragment

Most of procedures for the structural modifications of the oxazine fragment in SPO are based on the insertion of the substituent R into the naphthalene fragment. The substituent is most commonly introduced into this fragment already in the step of the preparation of the starting 1-nitroso-2-naphthol. The general scheme of the synthesis of SPO containing substituents in the oxazine fragment is given below.



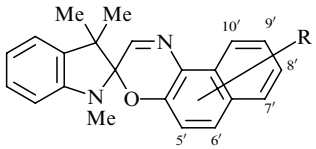
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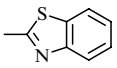
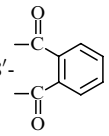
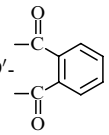
The localisation of the nitroso and hydroxy groups at positions 1 and 2 of the starting nitrosonaphthols **49** unambiguously determines the type of the resulting oxazine fragment as naphtho[2,1-*b*][1,4]oxazine (**50**). 1-Nitroso-2-naphthols occupy a prominent place among other aromatic *o*-hydroxynitroso compounds due both to their high stability (compared, for example, to *o*-nitrosophenols) and the fact that they can be readily prepared by nitrosation of the corresponding naphthols.

In recent years, the range of SPO of type **50** has been steadily extended due to the involvement of ever more complex nitrosonaphthols in this reaction (Table 3). This structural modification of SPO is one of the most commonly used processes, although the progress in this field is limited by the inaccessibility of some naphthols and the necessity of adapting the conditions of their nitrosation to the nature of the substituent.

Table 3. Substituted 1,3,3-trimethylspiro{indolino-2,3′-naphtho-[2,1-*b*][1,4]oxazines}.

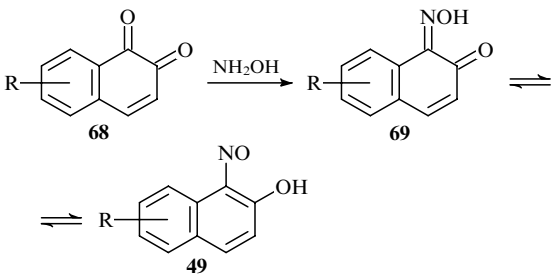


51–**67**

SPO	R	Ref.	SPO	R	Ref.
51	5′-OH	28, 58, 59	**60**	9′-SO_3Na	65
52	5′-CH_2OH	60, 61	**61**	8′-CN, 9′-CN	66, 68
53	5′-CO_2Me	62	**62**	8′-OH, 9′-CO_2Me	69
54	5′- 	59, 63	**63**	7′, 8′- 	19, 70
55	7′-NO_2	64	**64**	8′, 9′- 	68
56	8′-OH	65	**65**	9′-OH	58, 65, 71, 72
57	8′-COPh	19	**66**	10′-Me	68, 73
58	8′-CN	29, 66	**67**	10′-C_6H_4Me-*p*	68, 73
59	8′-SO_3Na	65, 67			

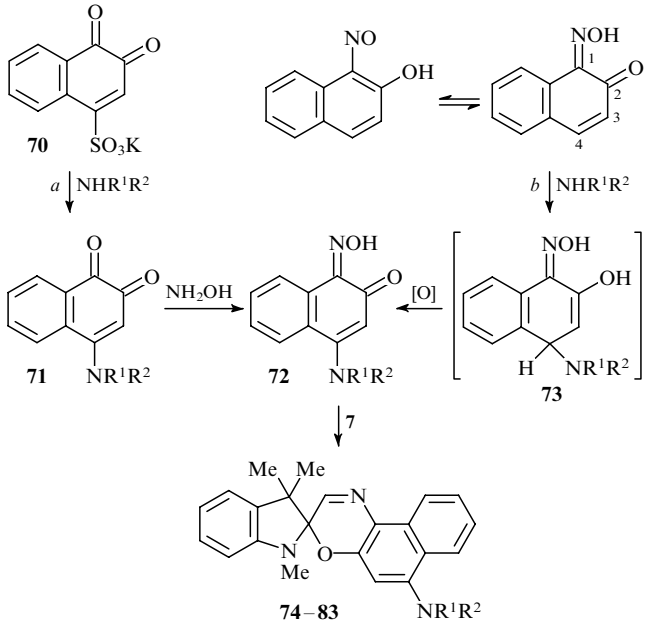
It is the difficulty to access 4-substituted 2-naphthols that accounts for the lack of 6′-substituted SPO in Table 3.

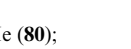
To close this gap, an original approach to 6′-substituted SPO has been developed. In this procedure, 1,2-naphthoquinones **68** rather than 2-naphthols were used as the source of 1-nitroso-2-naphthols. The reactions of compounds **68** with hydroxylamine afforded monooximes **69**, which are tautomers of nitrosonaphthols **49**.

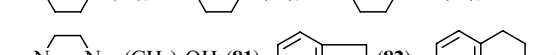


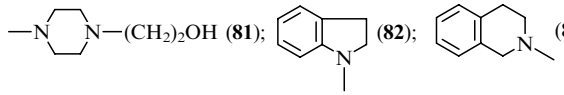
In the general case, 1,2-naphthoquinones are not more readily available compounds than naphthols. However, a number of their 4-substituted derivatives can be easily prepared by the nucleophilic substitution reaction of potassium 1,2-naphthoquinone-4-sulfonate (**70**). Thus, Rickwood and co-workers [20, 74] used various secondary amines as nucleophiles for the preparation of 4-amino-substituted 1,2-naphthoquinones **71**, which were then employed in the synthesis of 6′-amino-substituted SPO (Scheme 3, method *a*). These authors also developed a simplified (but much less universal) approach to the synthesis of the same compounds [20, 74, 75] on the basis of the reaction of 1-nitroso-2-naphthol, secondary amine and Fischer's base **7** without isolation of substituted nitrosonaphthol **72** (Scheme 3, method *b*). However, the mechanism of the insertion of the amino group is not entirely known. It was assumed [20] that the reaction involves the nucleophilic addition of secondary amine at position 4 of the quinone oxime tautomer of 1-nitroso-2-naphthol. Subsequent oxidation of intermediate **73** can occur under the action of the second 1-nitroso-2-naphthol molecule, which partially accounts for low yields.

Scheme 3

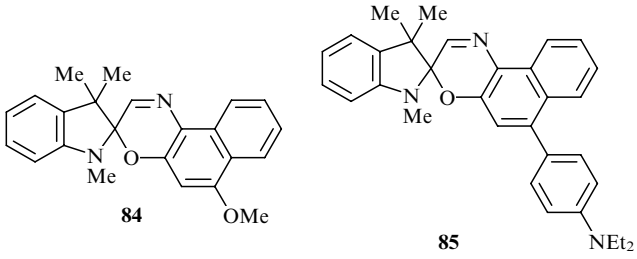


$-NR^1R^2$ = $-NMe_2$ (**74**); $-NEt_2$ (**75**);  (**76**);  (**77**);

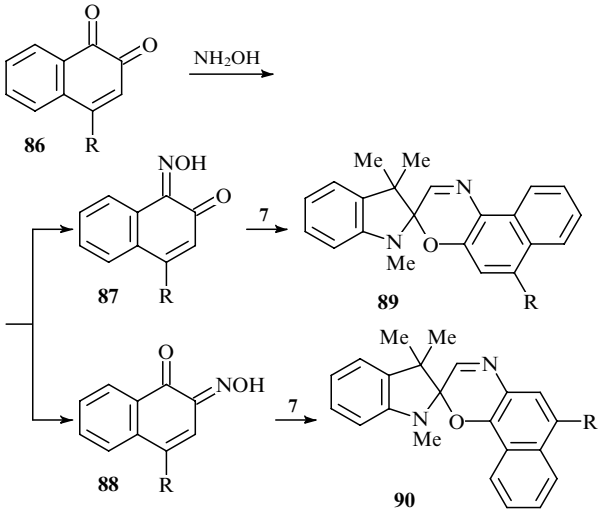
 (**78**); (**79**); (**80**);

 (**81**); (**82**); (**83**).

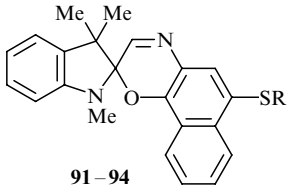
By combining both approaches, Rickwood and co-workers [20, 76] prepared a large series of 6′-amino-substituted SPO (**74**–**83**). Using the synthesis of SPO **84** (see Ref. 20) and **85** (see Ref. 76) according to the method *a* as examples, the authors demonstrated that O- and C-nucleophiles can be employed as nucleophilic reagents.



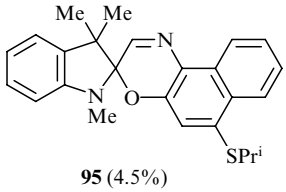
This scheme has been substantially refined in subsequent studies. In particular, NMR spectroscopic studies demonstrated that the reaction of 4-substituted naphthoquinones **86** with hydroxylamine is non-regioselective and affords, in the general case, a mixture of oximes **87** and **88**, which are difficult to separate.[16, 29, 77] The use of this mixture in the reaction with Fischer's base provides a possibility for the generation of two types of SPO, *viz*., naphtho[2,1-*b*][1,4]oxazines **89** and naphtho[1,2-*b*][1,4]oxazines **90**.



The predominance of a particular type of SPO depends on the ratio of the oximes in the mixture and their relative reactivities to Fischer's base. Thus, due to the low reactivities, 4-amino-substituted oximes **88** give the corresponding SPO **90** only in trace amounts.[29] However, if sulfur-containing substituents are inserted at position 4, compounds of type **90** (for example, **91**–**94**) rather than compounds of type **89** (for example, **95**) are generated as the major products in mixtures of SPO.[16]



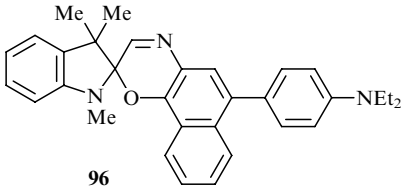
91–**94**



95 (4.5%)

R = Pr^i (**91**, 25.5%), C_6H_{11} (**92**), Ph (**93**), C_6H_4OMe-*p* (**94**).

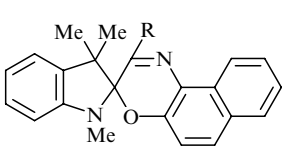
Apparently, these results have stimulated the researchers to revise the structure of compound **85**. In the recent patent,[78] structure **96** was assigned to this compound based on the results of X-ray diffraction study of the starting oxime.



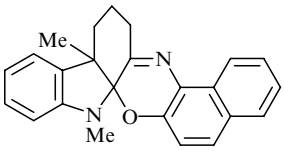
96

It should be noted that the synthetic efforts to prepare 6′-substituted SPO were compensated by good photochromic characteristics of most of these compounds, primarily, by high colourability and unusual spectral features.

A special type of the modification of the naphtho[2,1-*b*]-oxazine fragment involves the insertion of substituents at position 2′. For example, 2′-substituted SPO **97**–**100** were synthesised.[44, 79–81]



97–**99**



100

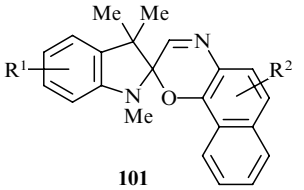
R = Me (**97**), Pr (**98**), Ph (**99**).

Unlike structurally similar SPP, SPO of this type do not exhibit photochromic properties at room temperature although short-lived coloured forms of some of these compounds were detected upon laser flash photolysis with nanosecond time resolution.[80]

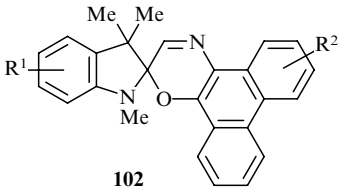
b. Aromatic annelation and heteroannelation

The need for the extension of the gamma of the photochromic characteristics of SPO provides a steady impetus to the synthesis of new types of SPO whose structures differ from the classical naphtho[2,1-*b*]oxazine structure **50**. This aim can be achieved by synthesising SPO with the use of aromatic and heterocyclic *o*-hydroxynitroso derivatives, for example, nitrosophenols, nitrosophenanthrols, *o*-hydroxynitrosoquinolines, *etc*., instead of 1-nitroso-2-naphthols. This type of structural modifications, which has received considerable attention already in early studies,[4, 6] was further developed in recent years.

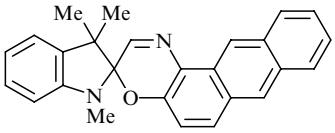
In particular, new derivatives belonging to the class of SPO characterised by aromatic annelation, such as naphtho[1,2-*b*]oxazines (**101**),[16, 82–84] phenanthro[9,10-*b*]oxazines (**102**),[81, 85] anthra[2,1-*b*]oxazines (**103**)[23] and benzooxazines (**104**),[44, 86] were synthesised. A procedure for the synthesis of a new representative of this type of SPO, *viz*., spirofluoroanthene[3,2-*b*]oxazine (**105**), was covered by a patent.[87]



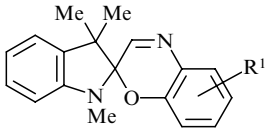
101



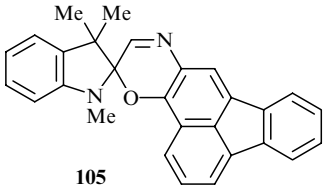
102



103



104

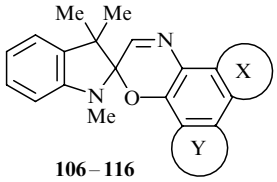


105

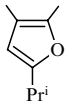
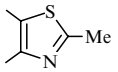
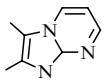
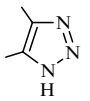
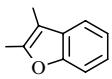
Heteroannelation of the benzooxazine fragment was particularly widely reflected in recent patents and publications. New compounds of this type are listed in Table 4.

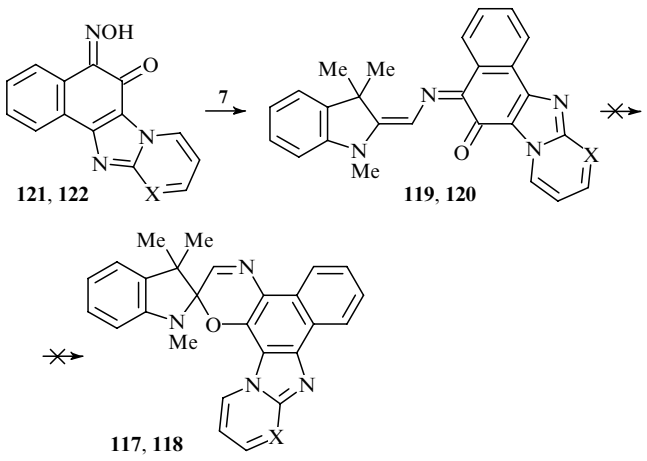
Interesting results were obtained by Lareginie *et al*.[77] In attempting to synthesise SPO **117** and **118** containing the annelated imidazo[1,2-*a*]pyridine and imidazo[1,2-*a*]pyrimidine rings, respectively, compounds **119** and **120** having open merocyanine structures were prepared instead of the expected compounds with spirocyclic structures.

Table 4. Heteroannelated SPO of the indoline series.



106–**116**

SPO	X	Y	Ref.	SPO	X	Y	Ref.
106		–	88	**112**	–		83
107		–	24, 89	**113**			29
108		–	24, 90	**114**			77
109		–	91	**115**			85, 95, 96
110		–	92–94	**116**			85
111	–		83				

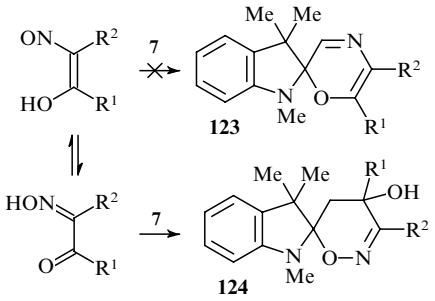


121, **122** **119**, **120** **117**, **118**

X = CH (**117**, **119**, **121**), N (**118, 120**, **122**).

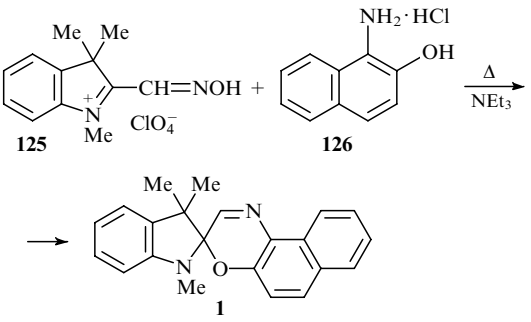
Compounds **119** and **120** are the only known examples of stable merocyanines of the spirooxazine series. Physicochemical and X-ray diffraction studies of these compounds provided valuable information on the probable three-dimensional and electronic structures of the short-lived coloured forms of SPO, which can usually be obtained only by indirect methods.[97–99]

In conclusion of this section, let us mention an interesting attempt to synthesise SPO **123**, which contains no nuclei annelated to the oxazine ring.[28] Unfortunately, the synthesis afforded 1,2-oxazines **124**, which do not exhibit photochromic properties.

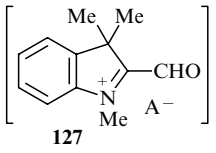


III. Synthesis of spirooxazines from 1-amino-2-naphthols and related compounds

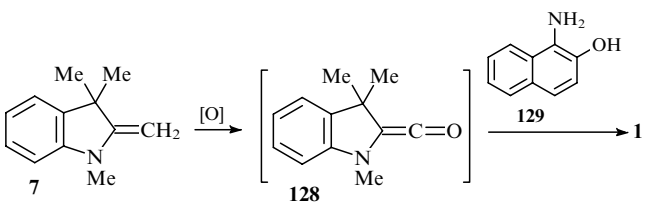
As early as 1971, when analysing various hypothetical approaches to spirocyclic photochromic compounds, Bertelson [2] noted that the oxazine ring of SPO could be, in principle, constructed by the reactions of carbonyl compounds with amines. The first step forward in this direction was made by Japanese scientists [100] who demonstrated that SPO **1** can be prepared by the reaction of 2-hydroxyiminomethyl-1,3,3-trimethylindoleninium perchlorate (**125**) with 1-amino-2-naphthol hydrochloride (**126**) in the presence of triethylamine.



Although the mechanism of this reaction remains to be studied, it seems rather probable that the reaction produces a carbonyl-containing intermediate of type **127**, which then interacts with the amino group.



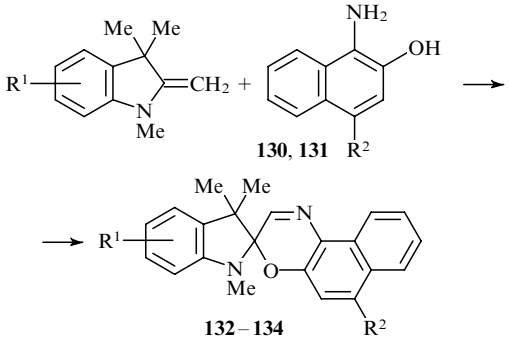
Minkin and co-workers [85, 101] have made an essential contribution to the development of this field of investigation. The Russian researchers found that the carbonyl-containing intermediate (to which the structure of ketene **128** was assigned), which can react with 1-amino-2-naphthol (**129**) to give SPO **1**, can be prepared by mild oxidation of Fischer's base **7**.[101]



Selenium dioxide and pyridinium chlorochromate were successfully tested as oxidising agents. However, the best results were obtained with the use of dimethyl sulfoxide promoted by the addition of sodium bicarbonate. The advantages of this approach over the classical 'nitroso' method are that it affords the reaction products in higher yields and gives rise to smaller amounts of impurities, which substantially facilitates the chromatographic purification of the products.

The use of annelated analogues of 1-amino-2-naphthols, such as 9-amino-10-phenanthrols and 1-amino-2-anthrol, instead of 1-amino-2-naphthols themselves, made it possible to prepare SPO of types **102** and **103**.[85, 101]

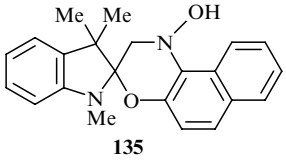
Additional advantages of the procedure under consideration were revealed in the study.[15] In particular, this procedure was employed for preparing SPO **132**–**134** starting from readily accessible aminonaphthols **130** and **131**.[102–104] These products contain strong electron-withdrawing substituents at position 6′ and possess good photochromic characteristics.



R^1 = H (**132**, **133**), 5-OMe (**134**);
R^2 = CN (**130**, **132**, **134**), $SO_2C_6H_4Me$-*p* (**131**, **133**).

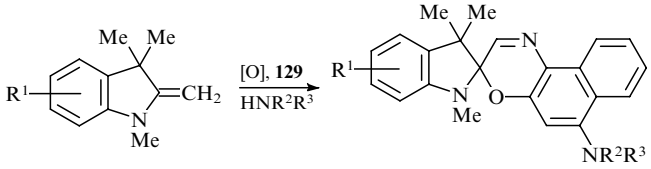
Yet another important advantage of this procedure is that the reactions can be carried out under much milder conditions. This made it possible to increase the yields of SPO **43** and **44**, which were prepared from bases of type **2** unstable under the reaction conditions (prolonged heating).[15]

These mild reaction conditions allowed the Russian researchers[§] to isolate stable intermediate **135** whose structure was established by NMR spectroscopy.



Compound **135** is rapidly converted into SPO **1** upon heating in different solvents. It is not inconceivable that this compound is also the direct precursor of SPO **1** in the 'nitroso' method (see structure **5**, Scheme 1), but this hypothesis calls for an additional verification.

Within the framework of this method, yet another unexpected result was obtained.[105] It appeared that oxidation of Fischer's base in the presence of secondary amines afforded (in much higher yields) 6′-amino-substituted SPO analogous to those prepared according to Scheme 3.



Since 1-amino-2-naphthol (**129**), unlike 1-nitroso-2-naphthol, cannot react with secondary amine by the Michael addition mechanism (Scheme 3, method *b*), the step in which the amino group is inserted into the molecule remains an open question.

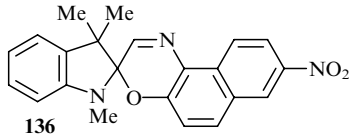
§ A V Koshkin, V Lokshin, O A Fedorova *Unpublished data*.

IV. Chemical reactions of spirooxazines

The syntheses of the first spirooxazines have presented difficulties due to which SPO had an unjust reputation of chemically unstable compounds.[4] However, these compounds can be subjected to various chemical transformation in spite of a certain instability, particularly, in the presence of water and acids. These transformations are considered below.

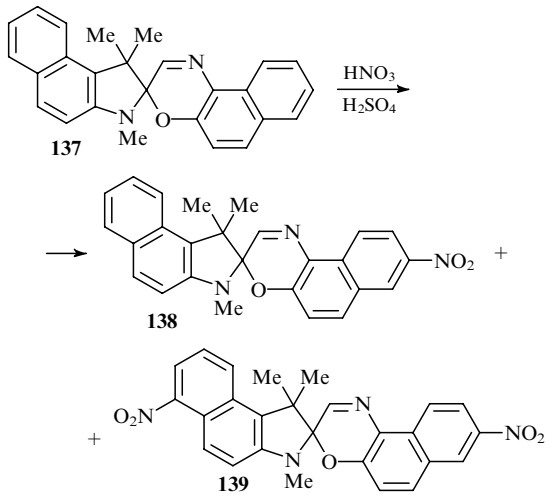
1. Electrophilic substitution of the hydrogen atom

Russian scientists made an essential contribution to investigation of this type of reactions of SPO.[64, 106, 107] In particular, they demonstrated that nitration of SPO **1** with nitric acid ($d = 1.35$ kg m^{-3}) in concentrated sulfuric acid afforded 8′-nitro-substituted derivative **136**.



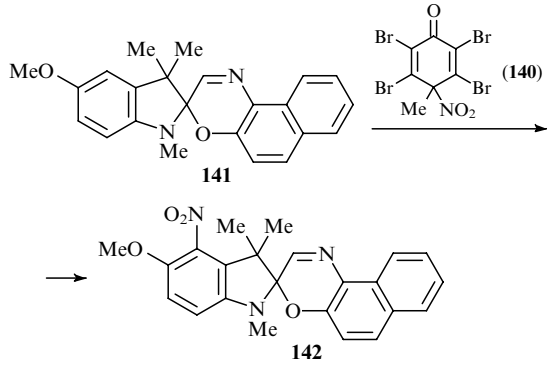
136

However, nitration of benzoannelated compound **137** under the same conditions gave rise to dinitro compound **139** along with the expected 8′-nitro derivative **138**.[106]



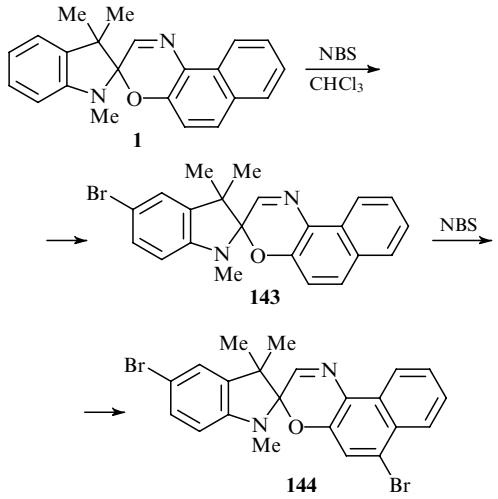
137 **138** **139**

Attempts to use a softer nitrating agent, *viz*., 2,3,5,6-tetrabromo-4-methyl-4-nitrocyclohexa-2,5-dien-1-one (**140**), failed.[29] However, the reaction of this reagent with SPO **141** containing the activated indoline fragment gave rise to 4-nitro derivative **142**.



141 **(140)** **142**

Bromination of SPO **1** with *N*-bromosuccinimide (NBS) proceeded initially at position 5 of the indoline ring. Further bromination of the resulting SPO **143** yielded 5,6′-dibromo derivative **144** in a mixture with by-products.[107]



1 **143** **144**

2. Synthesis of esters, amides and ethers

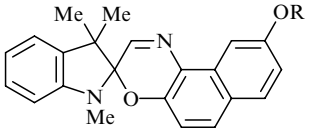
a. Acylation and alkylation of hydroxy-substituted SPO

Acylation of 9′-hydroxy-containing SPO **65** and its derivatives is the most widespread reaction of SPO. Acid chorides [60, 71, 72, 108] or acid anhydrides [109] can be employed as acylating agents, which are most often prepared *in situ* from the corresponding acids and dicyclohexylcarbodiimide (DCC).[40, 110–112] A series of acyl derivatives of SPO **65** are given in Table 5.

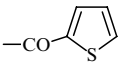
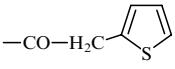
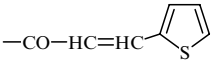
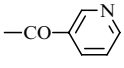
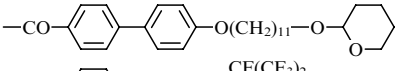
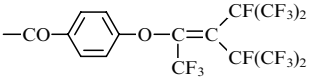
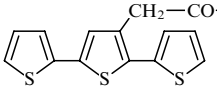
Analogous approaches are used for acylation of the hydroxy groups at positions 5 (see Refs 42 and 112) and 8′ (see Ref. 69).

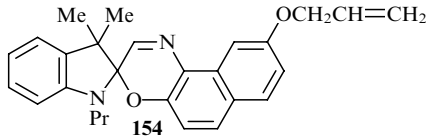
Alkylation of the HO groups of hydroxy-containing SPO is less well studied. Dürr *et al*.[72] synthesised SPO **154** and **155** by the treatment of the corresponding hydroxy derivatives with alkyl halides in anhydrous acetonitrile in the presence of potassium carbonate.

Table 5. Acyl derivatives of 9′-hydroxy-substituted SPO **65**.

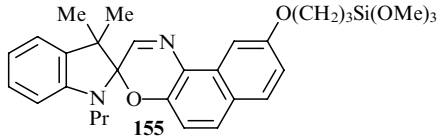


145–153

SPO	R	Ref.
145	—COC(Me)=CH$_2$	60, 72
146	—CO(CH$_2$)$_3$CO$_2$H	109
147		40
148		40
149		40
150		108
151		112
152		71
153		111



154

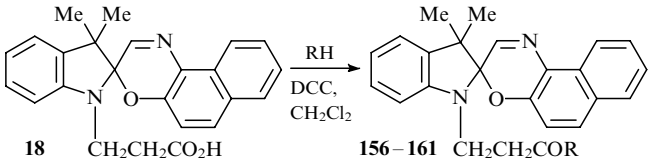


155

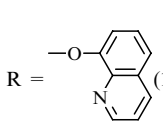
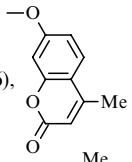
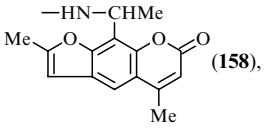
Dimethyl sulfate was successfully used for methylation of the hydroxy groups at positions 5′ and 8′.[59,69]

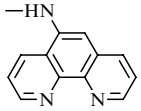
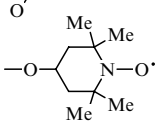
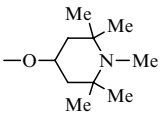
b. Reactions of carboxy-substituted SPO

N-Carboxyethyl-substituted SPO **18**, which was synthesised for the first time by Ono,[9] is a convenient reagent for the preparation of esters and amides. Various compounds of this type (**156**–**161**) containing luminescent, complex-forming or antioxidant fragments were synthesised by Chinese researchers.[36,113]



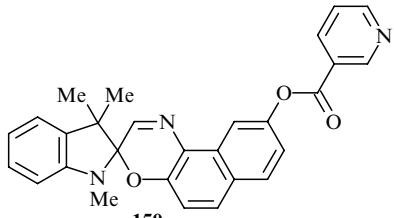
18 **156**–**161**

R =  (**156**),  (**157**),  (**158**),

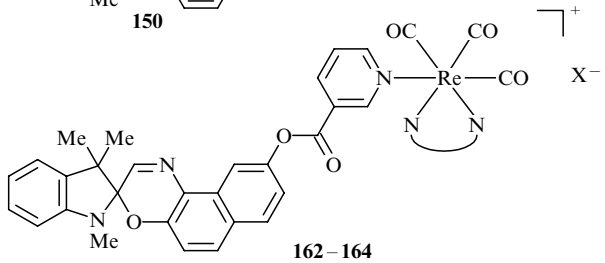
 (**159**),  (**160**),  (**161**).

3. Synthesis of coordination compounds

Recently, Chinese researchers[108] reported the preparation of stable crystalline complexes of SPO **150** with Re(I) salts with compositions $[Re(CO)_3(phen)(SPO)]ClO_4$ (**162**), $[Re(CO)_3(4,4'\text{-}Me_2bipy)(SPO)]ClO_4$ (**163**) and $[Re(CO)_3(4,4'\text{-}Bu^t_2bipy)(SPO)].PF_6$ (**164**) (phen is 1,10-phenanthroline, bipy is 2,2′-bipyridyl).



150



162–**164**

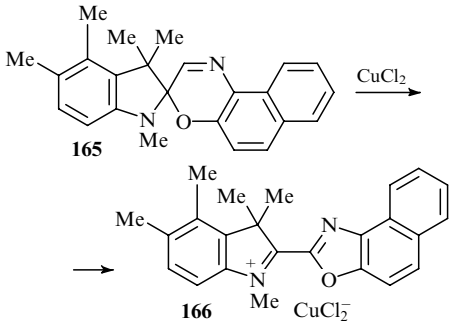
N N — phen (**162**), 4,4′-Me_2bipy (**163**), 4,4′-Bu^t_2bipy (**164**).

The structures of compounds **162**–**164** were confirmed by spectroscopic methods. In addition, the structure of compound **164** was established by X-ray diffraction analysis. Photocolouration of SPO was observed upon irradiation of compounds **162**–**164** in the absorption band of the organometallic fragment (~ 420 nm), which was attributed to the intramolecular energy transfer.

The synthesis of stable complexes of SPO of type **115** with $Ru(bipy)_2Cl_2$ was described in the earlier study.[85] However, attempts to isolate these compounds in the solid state failed.

In the studies,[114,115] the formation of stable luminescent adducts of the coloured form of SPO with metal salts in solution has been reported. In some cases, these reactions proceeded even without irradiation.[62] Nevertheless, the conclusions about the coordination nature of these compounds should be made with caution.

Indeed, Malatesta and co-workers[116,117] showed that SPO (for example, SPO **165**) can react with metal salts, for example, with $CuCl_2$, on heating through the redox mechanism to give compounds of type **166**.



165 **166**

Apparently, the naphthooxazole fragment, which is present both in molecule **166** and products of its transformations,[117] is responsible for the fluorescence observed.

Recently, analogous transformations have been found in the reactions of SPO **1** with silver salts[118] and lead salts.[119]

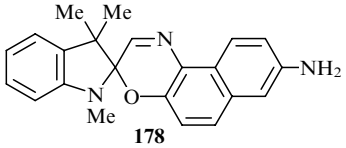
4. Reactions of hydroxymethyl- and formyl-substituted SPO

Hydroxymethyl derivative **52** proved to be very useful in studies of chemical transformations of SPO. French researchers[61,120] used this compound for the preparation of numerous SPO derivatives (Scheme 4), which are of interest not only as photochromes but also as precursors for the preparation of biphotochromic compounds (see below).

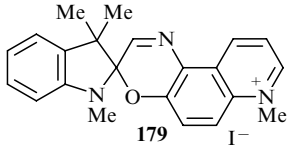
The key reaction in Scheme 4 involves mild oxidation of SPO **52** with periodinane **169** (Dess–Martin reagent) to give formyl derivative **170**. Compound **170** can be involved in different reactions at the aldehyde group, for example, in the Wittig and Knoevenagel reactions, which made it possible to prepare a series of vinyl derivatives **171**–**175**, which have an extended conjugation system and, as a consequence, possess unique photochromic characteristics.[120] The same formyl-substituted SPO **170** was used as the starting compound in the synthesis of compounds **176** and **177**, which contain substituents possessing properties of spin traps.[121,122]

5. Other reactions

Of other SPO transformations, reduction of nitro derivative **136** with hydrazine hydrate in the presence of Raney nickel giving rise to amino derivative **178**[123] and the preparation of salt-like SPO **179**, which unexpectedly exhibits photochromic properties in the crystalline state,[124] deserve notice.

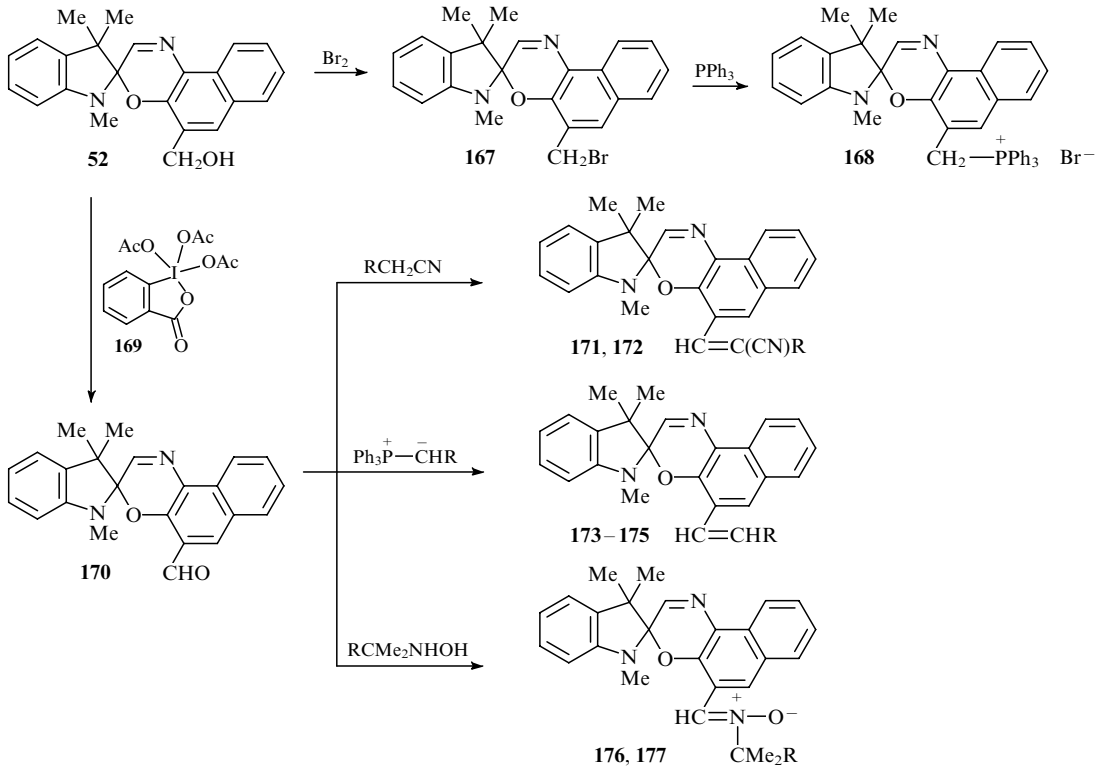


178



179

Scheme 4



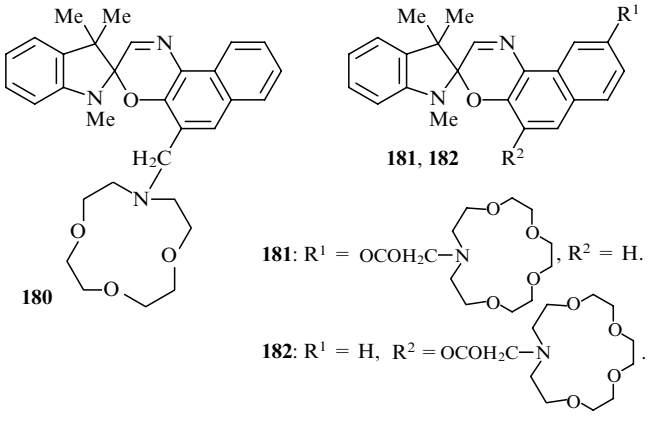
R = CO_2Et (**171**), CN (**172**, **175**), CO_2Me (**173**), CHO (**174**), Me (**176**), $PO(OEt)_2$ (**177**).

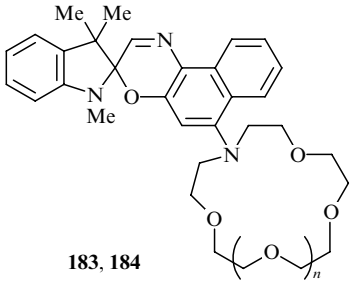
V. Spirooxazine-containing molecular systems

The synthesis of complex molecular systems involving covalently bound photochromic fragments is a promising field of the chemistry of SPO. These systems are increasingly employed as photomodulators, which can change their physicochemical characteristics under irradiation, thus influencing the structure and properties of their chemical environment.

1. Spirooxazine-containing crown ethers

The first compound of this type, *viz*., SPO **180**, was prepared by Japanese scientists.[125, 126] They introduced a macrocyclic fragment into the starting 3-hydroxymethyl-2-naphthol. Other approaches were used by the Russian–French research team,[58, 127–129] who have actively developed this area of investigation in recent years. In particular, compounds **181** and **182** were prepared by acylation of hydroxy-containing SPO **51** and **65**, respectively. The synthesis of SPO **183** and **184** was carried out according to a procedure shown in Scheme 3 (method *b*).





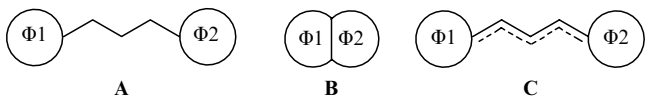
183: $n = 1$;
184: $n = 2$.

Substantial changes in the parameters of the photochromic transformations of crown-containing SPO in the presence of some metal cations were observed in virtually all studies. The recent comprehensive study [130] showed that the complex formation is a very complicated process.

2. Spirooxazine-containing biphotochromic systems

The term 'biphotochrome' was introduced by Dürr [131] to describe molecules containing two covalently bound photochromic units of the same or different types.

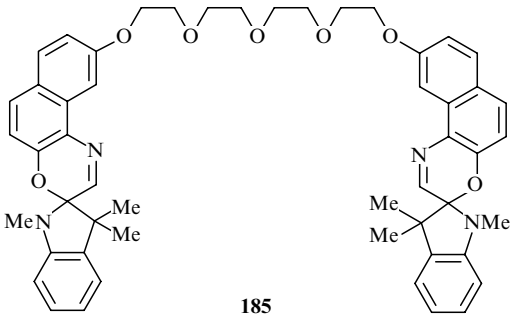
Depending on the mode of binding of two fragments, such compounds can be arbitrarily divided into three types, all having representatives of the spirooxazine series.



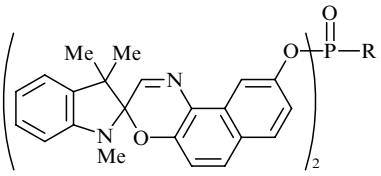
Φ1 and Φ2 are identical or different photochromic molecules.

The properties of compounds of the type **A** in which the photochromic units are linked *via* a non-conjugated chain are determined, to a large extent, by the type of the bridge. Thus, the polyether chain in compound **185** ensures the photomodulated affinity for Na^+ ions,[132] whereas the phosphorus-containing

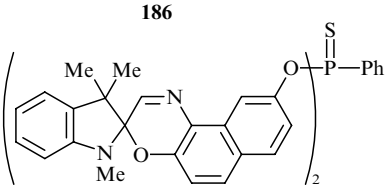
groups in SPO of types **186** and **187** enhance, in the authors' opinion, [133] their photostability.



185

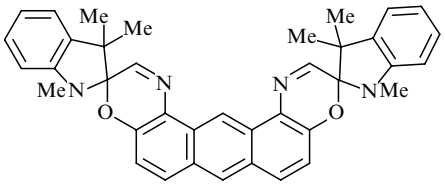


186

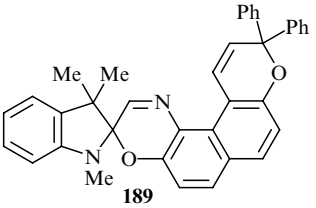


187

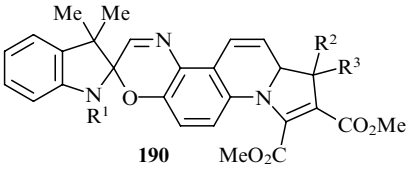
The major impetus for the synthesis of annelated biphotochromes of the type **B** containing common aromatic nuclei was the desired preparation of coloured forms possessing unusual spectral characteristics. However, since the photochromic fragments in these compounds are not independent, their simultaneous photoexcitation presents problems. Of three biphotochromic compounds of the type **B** considered below, *viz*., SPO–SPO **188**,[134, 135] SPO–chromene **189** (see Ref. 29) and SPO–dihydroindolizines of type **190**,[136] simultaneous excitation of both photochromic fragments was observed only for compounds **190**. As a result, the absorption spectra of the coloured forms of these compounds are shifted to the IR region.



188



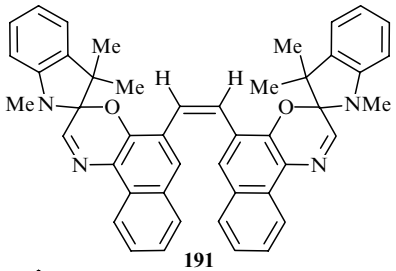
189



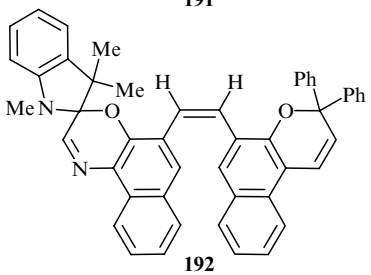
190

A series of biphotochromes of the type **C** in which the photochromic fragments are conjugated through the vinyl bridges have been described in the recent study.[61]

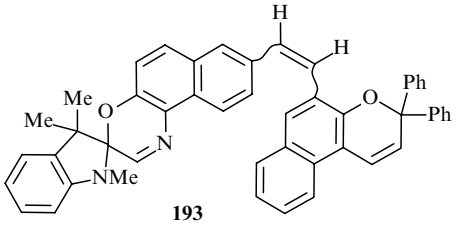
Compounds **191**–**194** containing the spirooxazine and chromene fragments were prepared from functionally substituted photochromes **168** and **170** by the Wittig reaction.



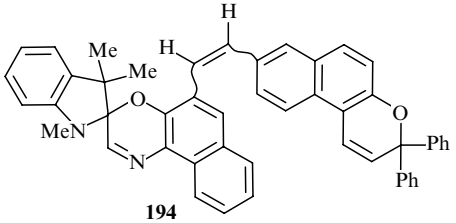
191



192

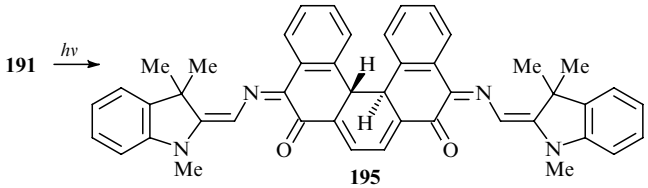


193



194

The photochromic behaviour of the above-mentioned compounds, which has been thoroughly studied later,[137–140] proved to be very complex. For example, not only successive opening of both oxazine rings but also the $Z \rightarrow E$ isomerisation and electrocyclisation to form compound **195** were observed for SPO **191** obtained in the *Z* configuration.[140]



195

3. Spirooxazine-containing polymers

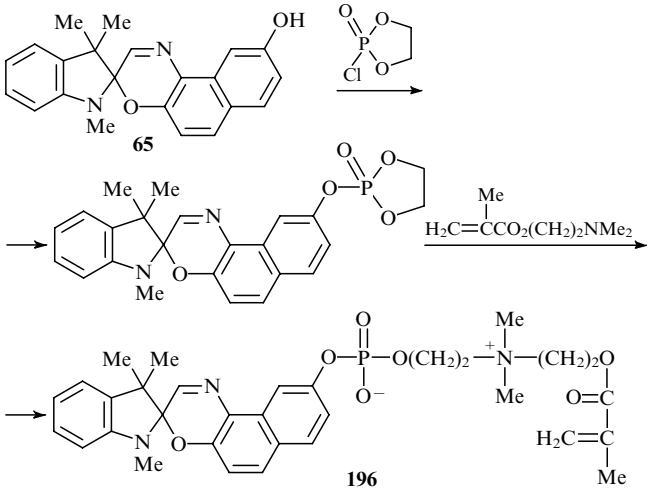
Most polymeric photochromic SPO-based materials are solutions of photochromes in the corresponding polymers. This procedure for the preparation of polymeric photochromic materials is much simpler than that proceeding *via* the covalent binding of SPO with polymers. However, the latter method has considerable advantages, in particular it:

— provides a higher concentration of the photochrome;

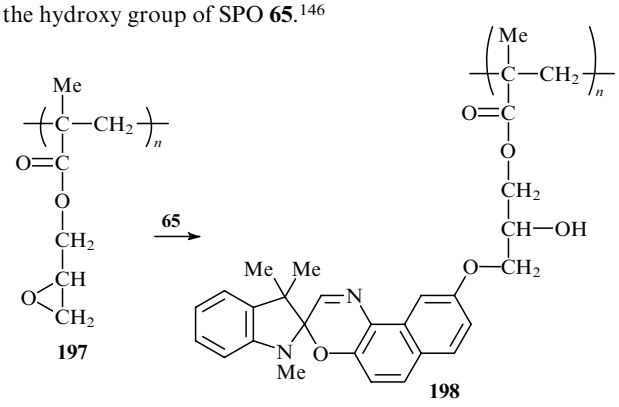
— hinders diffusion of the photochrome thus reducing the toxic risk in the course of the *in vivo* functioning of the material (for example, in contact lenses);

— improves the 'photomodulating' influence of the photochrome on the structure and characteristics of the polymer.

Most of the above-described spirooxazine-containing polymers belong to the class of polyacrylates. The corresponding monomers, for example, SPO **145**, are generally prepared by acylation of hydroxy-containing SPO.[60, 72, 112, 141] However, it is also possible to introduce functional groups capable of being polymerised into the indoline precursors.[142–144] A more complicated approach was used for the preparation of phosphorus-containing methacrylate monomer **196**. The polymer, which was prepared on the basis of this monomer, mimics the structure of phospholipid membranes.[145]



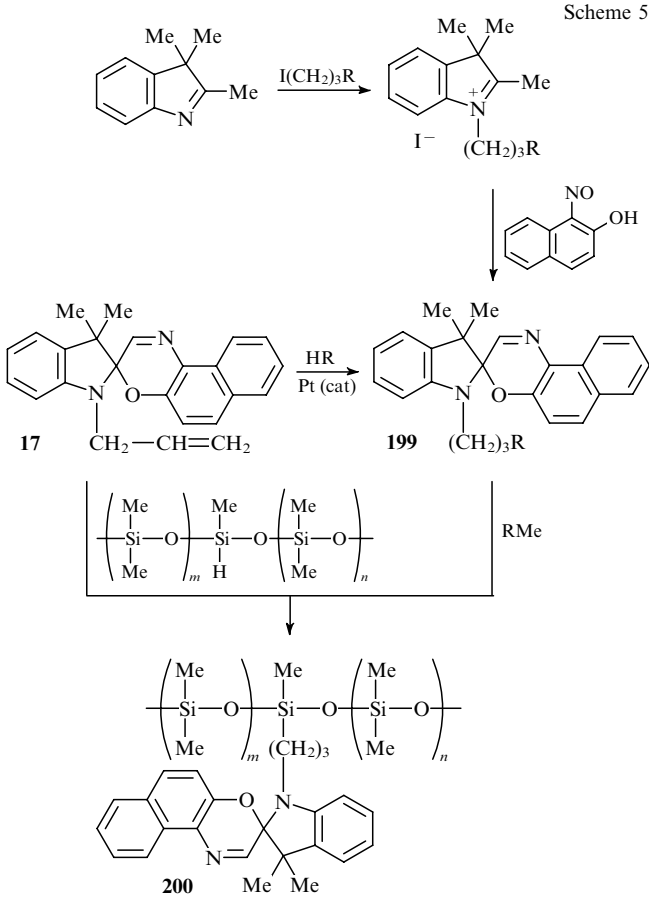
In addition to polymerisation (generally, radical) of spirooxazine-containing monomers, spirooxazine-containing polymers are also synthesised by the introduction of SPO into an available polymer containing functional groups. An example of this approach is the preparation of polymer **198** through the oxirane-ring opening of poly(glycidyl methacrylate) **197** under the action of the hydroxy group of SPO **65**.[146]



Polysiloxanes belong to another large class of spirooxazine-containing polymers. Studies of these polymers were initiated in the beginning of the 1990s by Krongauz and co-workers[142] and are being carried out actively by this research team[147–149] as well as by Japanese scientists.[84, 150, 151] The main approaches to the synthesis of the polymers of type **200** are given in Scheme 5.

The synthesis of spirooxazine-containing polysulfones[43] starting from amino-substituted SPO **30** was also described.

Scheme 5



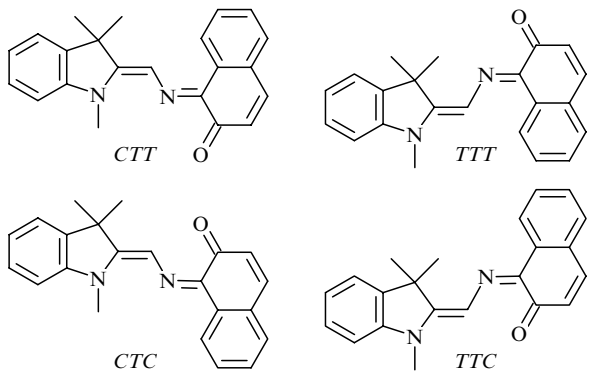
R = $Si(OEt)_2Me$.

VI. Structures of isomeric forms of spirooxazines and their interconversions in the ground state (solvatochromism and thermochromism)

The structures of spirooxazines were comprehensively studied by ^1H NMR spectroscopy, Raman spectroscopy,[152] quantum-chemical methods[98, 153, 154] and X-ray diffraction analysis.[16, 70, 77, 155–160]

The NMR spectra of spirooxazines are informative and allow one, with rare exception (for example, in the case of SPO **85** and **96**), to establish reliably the structures of the resulting compounds. Numerous publications[15, 35, 40, 58, 61, 106, 107, 161] and a special-purpose study[162] included the detailed assignments of the signals for protons and carbon atoms in the ^1H and ^{13}C NMR spectra of a broad spectrum of SPO. It should be noted that an unexpected correlation between the chemical shift of the 2′-carbon atom of SPO in the ^{13}C NMR spectra and the positions of the absorption maxima of their coloured forms was found in the study.[163]

According to the results of Hartree–Fock quantum-chemical calculations (HF 6-31G**/3-21G),[153, 154] four possible acyclic isomers of SPO, which are responsible for thermal and photo-induced colouration, adopt transoid configurations, *viz.*, *cis-trans-trans* (*CTT*), *trans-trans-trans* (*TTT*), *cis-trans-cis* (*CTC*) and *trans-trans-cis* (*TTC*), the *TTC* isomer being most stable.

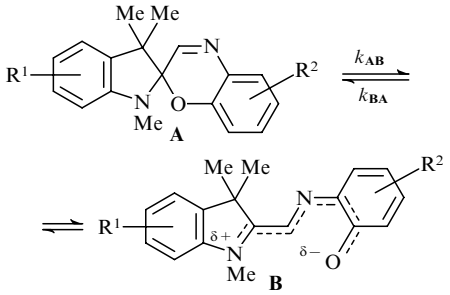


The X-ray diffraction data on the thermally unstable merocyanine form of SPO are scarce. The results of ^1H NMR spectroscopic study and X-ray diffraction analysis of open form **120**,

which was obtained in the synthesis of SPO **118**,[77] provided evidence for its *TTC* configuration.

In the ^{1}H NMR spectroscopic study of SPO **1**,[99] which was carried out directly on irradiation giving rise to the 90% conversion of the cyclic form, it was demonstrated that the *CTC* isomer can be formed in a small amount along with the most stable *TTC* isomer.

The tautomeric equilibrium between the cyclic **A** and merocyanine **B** forms in the ground state is typical of SPO in solutions. The **A** ⇄ **B** equilibrium was studied by ^{1}H NMR spectroscopy,[85, 95, 96] circular dichromism spectroscopy [164, 165] and spectrophotometry.[13, 96, 166–169]

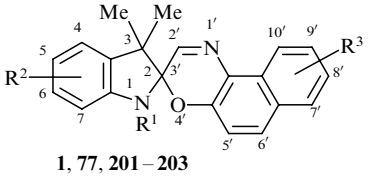


If the concentrations of the equilibrium forms **A** and **B** are sufficiently high that they can be reliably identified by NMR

Table 6. Equilibrium constants (K_e), standard enthalpies (ΔH°), free energies (ΔG°), entropies (ΔS°) of the equilibrium **A** ⇆ **B** and rate constants (k_{AB}) and activation energies (E_a^{AB}) of the thermal colouration reaction **A** → **B**.

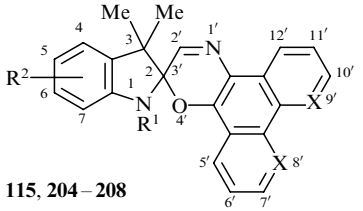
Compound	Solvent	$10^{-2}\,K_e$	ΔH° /kJ mol^{-1}	ΔG° /kJ mol^{-1}	ΔS° /J mol^{-1} K^{-1}	$10^{-2}\,k_{AB}$ /s^{-1}	E_a^{AB} /kJ mol^{-1}	Ref.
1 [a]	toluene	0.0012	21.7	28.0	−21.0	0.00028	69.0	166
	ethanol	0.011	20.9	22.6	−5.6	0.0025	102.0	166
77 [a]	toluene	0.06	18.0	18.4	−1.3	0.0021	82.4	166
	ethanol	0.58	15.0	12.8	7.4	0.336	56.0	166
201 [a]	"	0.061	17.4	18.4	−3.3	0.017	92.0	168
202 [a]	"	0.04	20.5	19.4	3.7	0.0012	100.0	168
203 [a]	"	0.24	17.4	14.9	8.4	0.0017	118.0	168
204 [a]	toluene	0.51	9.6	13.1	−11.7	0.07	76.1	166
	ethanol	1.1	10.9	11.2	−1.0	3.52	76.5	166
	"	0.8	10.9	12.0	−3.7	3.5	77.0	168
205 [a]	"	0.1	13.7	11.4	7.7	3.2	86.0	168
115 [b]	toluene	2.4	12.1	9.1	6.8	0.39	–	96
	ethanol	7.8	10.8	6.3	15.2	0.90	–	96
	methanol	8.8	8.5	6.0	8.4	1.02	85.7	96
	acetonitrile	9.0	4.3	5.9	−5.4	5.25	–	96
206 [b]	toluene	8.4	3.6	6.1	−8.4	0.87	–	96
	ethanol	28.1	2.5	3.1	−2.0	2.65	–	96
	methanol	34.1	1.0	2.6	−5.5	3.28	79.3	96
	acetonitrile	23.3	1.1	3.6	−8.4	12.51	–	96
207 [b]	heptane	2.5	11.7	9.1	8.8	0.25	83.9	96
	toluene	7.5	8.4	6.4	6.8	0.97	74.5	96
	ethanol	30.6	3.6	2.9	2.3	0.58	100.5	96
	methanol	43.2	1.8	2.1	−1.2	0.75	101.5	96
	acetonitrile	44.6	0	2.0	−6.8	3.74	83.8	96
208 [b]	heptane	2.3	13.4	9.3	13.9	0.25	89.8	96
	toluene	8.6	8.1	6.0	6.8	1.24	78.6	96
	ethanol	33.8	2.7	2.7	0.1	0.59	102.4	96
	methanol	45.3	1.6	1.9	−1.2	0.82	115.3	96
	acetonitrile	49.3	0	1.7	−5.7	3.96	83.9	96

[a] For these SPO, K_e and k_{AB} were determined at 298 K. [b] For these SPO, K_e and k_{AB} were determined at 296 K.



1, **77**, **201**–**203**

Compound	R^1	R^2	R^3
1	Me	H	H
77	Me	H	6′-piperidino
201	Et	H	H
202	Me	H	8′-CO_2Me
203	Me	5-Me, 6-Me	8′-COEt



115, **204**–**208**

Compound	R^1	R^2	X
115	Me	H	N
204	Me	H	CH
205	Pr^i	H	CH
206	$C_{16}H_{33}$	H	N
207	Me	5-OC_9H_{19}	N
208	Me	5-$OC_{16}H_{33}$	N

spectroscopy, the equilibrium constants can be determined (K_e). Due to the presence of the prochiral sp^3-hybridised carbon atom in the indoline ring, the kinetics of the reaction $\mathbf{A} \rightleftarrows \mathbf{B}$ can be studied by dynamic ^1H or ^{13}C NMR spectroscopy (from the shapes of the signals of the diastereotopic methyl groups bound to this carbon atom). The potential barrier is determined by the energy of the $C_{spiro}-O$ bond cleavage.

For most of SPO, the equilibrium $\mathbf{A} \rightleftarrows \mathbf{B}$ is substantially shifted to the cyclic isomers **A**. In these cases, it is most convenient to monitor the equilibrium by spectrophotometry, which enables one to detect the coloured form at very low concentrations (lower than 1%). If the molar extinction coefficients (MEC) of acyclic isomers are known, the equilibrium constant and thermodynamic parameters of the equilibrium can also be determined.

The available published data allow one to follow the influence of the molecular structure of various indolinospirooxazines on the quantitative characteristics of the equilibrium $\mathbf{A} \rightleftarrows \mathbf{B}$ (Table 6). In the series of SPO containing aromatic or heterocyclic fragments annelated to the oxazine nucleus, the equilibrium constant increases on going from naphthalene to phenanthrene and phenanthroline. The insertion of electron-donating groups (OAlk) at position 5 of the indoline fragment leads to an increase in the equilibrium concentration of the merocyanine form in solutions of SPO.

The equilibrium position is sensitive to the changes in the polar properties of the solvents and temperature of the solutions. In polar solvents, the equilibrium is shifted to acyclic isomers. The equilibrium constant increases as the temperature is raised. The temperature dependence of the equilibrium constant enables one to determine the thermodynamic characteristics of the equilibrium, *viz*., the standard enthalpy (ΔH°), free energy (ΔG°) and entropy (ΔS°) (see Table 6).

The phenomenon related to the changes in the positions and sometimes in the intensities of the bands in the electronic absorption or fluorescence spectra of solutions due to changes in the properties of the solvent (polarity, tendency to be involved in specific interactions) is called solvatochromism.[170] The solvatochromism of spirooxazines is associated with the influence of the nature of the solvent on the position of the equilibrium $\mathbf{A} \rightleftarrows \mathbf{B}$. The solvatochromic effect of SPO can be estimated from the change in the equilibrium constant in passing from one solvent to another (at the same temperature). As can be seen from Table 6, the largest changes in the equilibrium constant on going from weakly polar to polar solvents are observed for SPO of the phenanthroline series. The strong solvatochromic effect is observed also for 5-alkyloxy-substituted compounds **207** and **208**.

Thermochromism is a reversible change in colour of a compound due to a change in temperature in the range limited by the boiling point of the solvent (for solutions) or melting point (for solids).[171] Apparently, the temperature dependence of the equilibrium constant between the cyclic and merocyanine forms of SPO in solutions is an indication that the corresponding SPO are thermochromes, *viz*., compounds exhibiting thermochromism, and the thermochromic effect can be estimated from the standard enthalpy of the equilibrium. How fast the colour changes following the change in temperature, in particular, how fast solutions of SPO become coloured with increasing temperature, depends on the rate of attainment of the equilibrium. For SPO, $k_{\mathbf{BA}} > k_{\mathbf{AB}}$, *i.e*., thermal colouration is the rate-limiting process for the attainment of the equilibrium. Hence, the activation energy ($E_a^{\mathbf{AB}}$) of the process $\mathbf{A} \rightarrow \mathbf{B}$ can be rather accurately determined from the temperature dependence of the rate constant of colouration $k_{\mathbf{AB}}$. If the preexponential factors in the Arrhenius equation have close values, the larger is $E_a^{\mathbf{AB}}$, the more pronounced is the temperature dependence of $k_{\mathbf{AB}}$ for SPO. Hence, the thermochromic effect in SPO of the phenanthroline series is more pronounced in non-polar solvents, whereas the rate of the colour change with temperature is higher in alcohols (see Table 6).

VII. Spectral properties of spirooxazines

1. Electronic absorption spectra of cyclic forms of spirooxazines

Electronic absorption spectra of spirooxazines are characterised by long-wavelength absorption with maxima predominantly in the region of 330–380 nm and molar extinction coefficients (MEC) of 4000–20 000 litre mol^{-1} cm^{-1} (Fig. 1, Table 7). The effect of the substituents on the spectral characteristics of spirooxazines is associated with the structural features of SPO molecules, *viz*., with the presence of two acoplanar fragments, heterocyclic and oxazine responsible for photochromism.

The structural simulation showed that the electronic absorption spectra of SPP, which are structural analogues of SPO, can be considered with a certain degree of approximation as linear combinations of the absorption spectra of the constituent fragments. This approximation is possible because the fragments weakly interact with each other due to acoplanarity. The long-wavelength absorption bands are assigned to the photochemically 'active' pyran moiety, whereas the short-wavelength bands are assigned to the heterocyclic moiety.[173] An analogous approach was used [13, 166] for the interpretation of the absorption spectra of SPO. In particular, the absorption spectrum of SPO **1** in ethanol has a group of long-wavelength bands with maxima at 345 and 317 nm, which were assigned to electron transfers in the naphthooxazine moiety, and bands with maxima at 297 and 235 nm, which were assigned to transitions in the heterocyclic fragment.[13]

The validity of this assignment was confirmed by a comparison of the absorption spectra of solutions of SPO containing substituents in the heterocyclic and oxazine fragments, respectively. As can be seen from Table 7, the substituents in the oxazine fragment of spiroindolinonaphthooxazines exert a more substantial effect on the positions of the long-wavelength absorption bands than the substituents in the indoline moiety. The spectral range of changes in the positions of the long-wavelength absorption maxima of SPO containing substitutents in the naphthooxazine moiety with respect to unsubstituted SPO **1** is ~ 40 nm, whereas this range for SPO containing substituents in the indoline fragment is only 3 nm (cyclohexane).

The effect of substituents in the oxazine moiety of SPO on the positions of the absorption maxima is determined by their electron-donating and electron-withdrawing properties. Compounds containing electron-donating groups at positions 5′ and 9′ are characterised by short-wavelength (with respect to unsubstituted SPO **1**) shifts of the maxima of the long-wavelength absorption bands, whereas compounds containing electron-donating groups at positions 6′ and 8′ are characterised by the corresponding long-wavelength shifts. Electron-withdrawing sub-

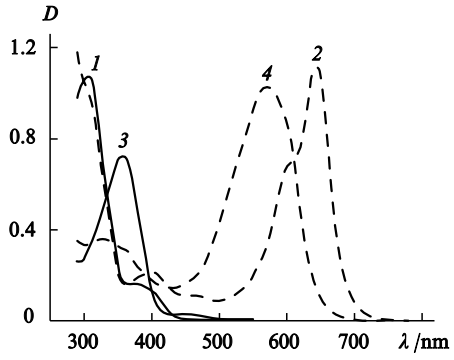
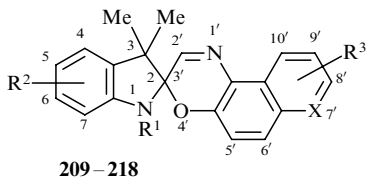


Figure 1. Electronic absorption spectra of SPO **217** in ethanol ($c = 1.1 \times 10^{-4}$ mol litre^{-1}, $T = 293$ K) (*1*, *2*) and SPO **29** in toluene ($c = 3.4 \times 10^{-5}$ mol litre^{-1}, $T = 293$ K) (*3*, *4*).
Curves *1*, *3* were measured before irradiation; curves *2*, *4* were recorded after irradiation with light at $\lambda = 365$ nm.

Table 7. Positions of the absorption maxima (λ_{max}) and molar extinction coefficients (ε_{max}) of the cyclic isomers **A** of spirooxazines.

Compound	λ_{max} /nm (ε_{max} /litre mol^{-1} cm^{-1})					Ref.	Compound	λ_{max} /nm (ε_{max} /litre mol^{-1} cm^{-1})					Ref.
	cyclo-hexane	toluene	ethanol	methanol	aceto-nitrile			cyclo-hexane	toluene	ethanol	methanol	aceto-nitrile	
1	320 (7600)	319 (7640)	318 (6450)	318 (6800)	317 (6600)	172	**212**	336 (5200)	337 (6020)	334 (6010)	334 (7580)	337 (5520)	172
	349 (5020)	348 (5410)	347 (4550)	347 (4710)	347 (4480)			372sh (2610)	376sh (2890)	375 (3660)	375sh (3920)	372sh (2540)	
141	318 (10330)	318 (11130)	317 (10640)	316 (9280)	316 (8900)	66	**133**	366 (9320)	368 (8612)	367 (9450)	366 (14690)	366 (8460)	66
	346 (5780)	347 (6280)	348 (6060)	347 (5180)	346 (4810)		**132**	367 (7710)	368 (7300)	369 (7850)	369 (7560)	368 (7370)	66
29	347 (21910)	356 (21490)	364 (21650)	—	367 (20210)	66	**134**	369 (8560)	372 (7770)	371 (7360)	370 (7260)	369 (7950)	66
51	340 (8740)	340 (9060)	339 (9100)	337 (7740)	—	66	**55**	—	—	358	—	—	64
52	323 (8990)	323 (7810)	322 (7830)	321 (9500)	319 (7140)	172	**213**	366 (3970)	367 (3940)	366 (3920)	365 (4110)	365 (3160)	172
	348sh	348sh	348sh	348sh	348sh		**214**	354 (5020)	355 (4610)	353 (4840)	342 (4200)	352 (4130)	66
209	319 (10730)	320 (9710)	318 (10420)	317 (8350)	318 (10400)	172	**58**	348sh (4530)	348sh (4510)	348 (4330)	348 (4040)	348 (4890)	66
	343sh	344sh	344sh	344sh	344sh		**215**	348 (4420)	348 —	348sh —	348sh (3990)	348sh (4390)	66
170	386 (4030)	389 (3720)	292	357sh (4320)	389 (4120)	66	**136**	356 (13300)	352 (9920)	356 (11710)	356 (12640)	356 (11970)	66
	404 (3540)	406 (3190)	389 (1870)	400sh (1780)	404 (3580)		**216**	336 (9810)	337 (8580)	337 (8900)	336 (8580)	334 (9500)	66
210	387 (4000)	389 (3640)	357 (3500)	357sh (4340)	389 (3660)	172	**217**	321 (10780)	323 (9780)	322 (9260)	323 (10030)	321 (11530)	66
	405 (3450)	406sh (3190)	400 (2460)	400sh (2130)	—		**61**	363 —	364 (4370)	365 —	365 (4560)	363 (4490)	172
174	311 (21560)	316 (22440)	319 (25600)	317 (23240)	314 (26080)	172		379 —	382 (3990)	379 —	379 (4090)	379 (4070)	
	389sh (2830)	389sh (3460)	400 (2740)	420 (2470)	400 (2570)		**218**	346 (5150)	347 (4890)	345 (4400)	346 (4440)	345 (4630)	172
53	385 (4340)	382 (4020)	402 (6470)	398 (5210)	403 (5360)	66		365 (3740)	364sh (3590)	359 (3500)	360sh (3530)	360sh (3590)	
	407sh (3760)	412 (3090)					**204**	298 (14370)	299 (13280)	285 (17890)	285 (16310)	296 (10520)	172
175	389 (2840)	386 (2930)	378 (3010)	378 (2740)	374 (2930)	172		344 (7130)	344 (7120)	344 (6950)	342 (6280)	342 (5760)	
211	376 (2980)	378 (3100)	376 (3430)	374 (3060)	372 (3250)	66		375 (4970)	375 (5090)	373 (5000)	373 (4480)	374 (3990)	
172	349 (20260)	354 (20890)	348 (19750)	345 (19010)	344 (18720)	172	**115**	—	344 (5900)	345 (5890)	344 (5810)	343 (6030)	96
	432 (2170)	435 (2430)	432 (1990)	431 (1830)	424 (2080)		**206**	—	347 (5980)	347 (5710)	347 (5650)	345 (5690)	96
77	363 (10660)	364 (11710)	365 (10370)	364 (12700)	364 (10800)	66	**207**	345[a] (5560)	345 (5420)	348 (5490)	348 (5790)	351 (5880)	96
							208	349[a] (5670)	345 (5410)	350 (5400)	347 (5680)	351 (5800)	96

[a] Heptane as the solvent.



209–**218**

Compound	R^1	R^2	R^3	X
209	Me	5-OMe	5′-CH_2OH	CH
210	$C_{16}H_{33}$	H	5′-CHO	CH
211	Me	5-OMe	5′-CH=CHCN	CH
212	Me	H	6′-SC_6H_4OMe-*p*	CH
213	Me	H	8′-OMe	CH
214	Me	H	8′-Br	CH
215	Me	5-OMe	8′-CN	CH
216	Me	H	9′-OMe	CH
217	Me	5-OMe	9′-OMe	CH
218	Me	H	H	N

stituents at positions 5′, 6′, 7′, 8′ and 9′ cause long-wavelength shifts of the absorption maxima in the spectra of solutions of SPO.

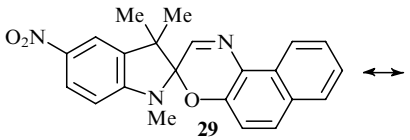
The electronic absorption spectrum of SPO **172** is characterised by an unusually broad long-wavelength absorption region due to a band with a weakly pronounced maximum at 430 nm. Conceivably, this absorption can be assigned to the intramolecular charge transfer from the naphthooxazine ring to the CN groups *via* the vinyl chain.

An extension of the π system of the oxazine fragment upon benzoannelation leads to a shift of the absorption boundary to the long-wavelength region. The electronic absorption spectrum of SPO **204** of the phenanthrene series has an additional maximum at 375 nm (toluene) compared to the absorption spectrum of naphtho derivative **1**, which is the manifestation of the vibrational nature of the long-wavelength absorption band belonging to the modified phenanthrene system.[174] This effect is even more pronounced in the case of anthracene derivative **103**. The spectrum of the latter compound has an additional long-wavelength vibrational maximum at 427 nm (heptane).[175]

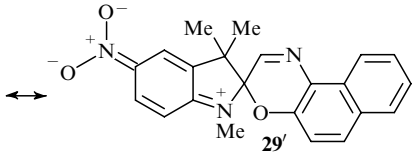
The modifications of the heterocyclic moiety of SPO by the replacement of the indoline fragment with the spatially hindered (SPO **40**[17]) or saturated (SPO **43**,[51] **44**[17]) azaheterocycles lead to substantial changes in the position of the long-wavelength absorption band.

Nevertheless, substituents in the indoline fragment of SPO can exert an effect on the position of the long-wavelength absorption maximum assigned to the transfer in the oxazine fragment. This effect depends on the nature of the substituents in both moieties of SPO. For example, the insertion of the methoxy group at position 5 of the indoline fragment has virtually no effect on the position of the long-wavelength absorption band in the case of SPO devoid of substituents in the naphthooxazine fragment (*cf.* **1** and **141**, Table 7), whereas such an insertion leads to a small (1–4 nm) long-wavelength shift in the case of 6′-cyano-substituted SPO (*cf.* **132** and **134**) and a noticeable short-wavelength shift by 13 nm in the spectra of 9′-methoxy-substituted SPO (*cf.* **216** and **217**).

In most cases, the electronic absorption spectra of SPO are independent of the polarity of the solvents and their ability to be involved in specific interactions (see Table 7). In this connection, noteworthy is the spectrum of 5-nitro-substituted SPO **29**. The maximum of long-wavelength absorption in the spectra of solutions of this compound is shifted bathochromically as the polarity of the solvent is increased. Apparently, this fact is attributed to the enhancement of resonance stabilisation of bipolar structure **29′** with increasing polarity of the solvent. This shift was not observed in the spectrum of 8′-nitro-substituted SPO **136**.



29

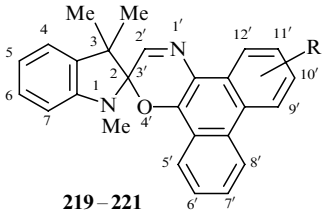


29′

2. Electronic absorption spectra of the coloured forms of spirooxazines

The spectra of the coloured forms of SPO show absorption in a substantially longer-wavelength region than the spectra of their cyclic isomers. The maxima of the bands are observed in the region of 480–670 nm and the bands are much more intense (40 000–80 000 litre mol^{-1} cm^{-1}; see Fig. 1, Table 8). Under normal conditions, the long-wavelengths bands in the stationary absorption spectra have an asymmetrical shape, which is manifested as a shoulder on the short-wavelength side (SPO **132**) or, more rarely, on the long-wavelength side (SPO **51**) relative to the maximum of the band. The position of the shoulder depends on the nature of the solvent (*cf.* SPO **29** and **216**). This effect is a consequence of the fact that the long-wavelength transition of the most stable *trans* isomer of the merocyanine form is vibrational in nature rather than results from the overlapping of bands of several stereoisomers.

The spectral characteristics of the coloured forms of SPO are sensitive to structural modifications and, unlike those of the cyclic forms, depend substantially on the substituents not only in the oxazine moiety of SPO but also in the heterocyclic fragment due to conjugation of both fragments occurring after the ring opening. The positions of the absorption maxima and the molar extinction coefficients (MEC) of the coloured forms **B** of a number of the above-considered spirooxazines and new SPO **219**–**221** are given in Table 8.



219–**221**

R = 9′-NO_2 (**219**), 10′-NO_2 (**220**), 11′-NO_2 (**221**).

The electron-donating substituents at positions 5′, 6′ and 9′ of the naphthooxazine moiety of spiroindolinonaphthooxazines cause short-wavelength shifts of the maxima of the absorption bands of the open form, whereas the presence of such substituents at position 8′ leads to long-wavelength shifts. Electron-withdrawing groups at positions 5′–9′ cause a long-wavelength shift of this maximum. By contrast, the insertion of electron-donating substituents into the indoline fragment of SPO leads to a long-wavelength shift of the absorption maximum, whereas the introduction of electron-withdrawing substituents causes a short-wavelength shift. The most essential spectral changes occur upon the insertion of a substituent at position 5 of the indoline fragment and at position 6′ of the naphthooxazine fragment.

Benzoannelation of the naphthooxazine fragment causes a slight shift of the absorption maximum of the coloured form. Thus, benzoannelation at positions 5′, 6′ (SPO **204**) leads to a short-wavelength shift, benzoannelation at positions 8′, 9′ (SPO **103**) causes a long-wavelength shift, whereas benzoannelation at positions 7′, 8′ (according to the results of the study[176]) has virtually no effect on the absorption spectrum (it remains similar to the spectrum of the form **B** of SPO **1**).

On going from naphthalene SPO **1** and phenanthrene SPO **204** to quinoline SPO **218** and phenanthroline SPO **115**, respectively, no noticeable spectral changes occur in absorption of the merocyanine forms.

In general, the spectral changes that are observed for a series of SPO and are associated with the insertion of substituents into the acyclic isomers **B** of spiroindolinonaphthooxazines, are typical also of other SPO of the indoline series. Thus, the introduction of the NO_2 group at positions 9′, 10′ or 11′ of phenanthrene derivatives of SPO leads to a long-wavelength shift of the absorption maximum of the coloured form.[177] Analogous changes occur also upon the introduction of the alkyloxy substituent at position 5 of the indoline fragment of phenanthroline-containing SPO **207** and **208** (see Table 8).

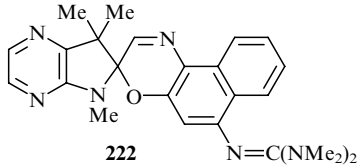
The replacements of the indoline fragment by the azabicycloalkane (SPO **40**–**42**),[46–49] piperidine (SPO **43**),[51] homoazaadamantane (SPO **44**)[17] or dibenzooxazepine (SPO **48**)[18] fragments cause short-wavelength shifts of absorption bands of acyclic isomers of SPO. In the case of SPO **40**–**42**, these shifts are associated with disruption of coplanarity resulting in the absence of conjugation between the lone pair of the nitrogen atom and the

Table 8. Positions of the absorption maxima (λ_{max}) and molar extinction coefficients (ε_{max}) of the coloured forms **B** of spirooxazines.

Compound	λ_{max} /nm (ε_{max} /litre mol^{-1} cm^{-1})					Ref.	Compound	λ_{max} /nm (ε_{max} /litre mol^{-1} cm^{-1})					Ref.
	cyclohexane	toluene	ethanol	methanol	acetonitrile			cyclohexane	toluene	ethanol	methanol	acetonitrile	
1	556	596	610	613	602	172	**134**	647	661	651	649	654	66
	578sh	565sh	572sh	573sh	565sh				(65870)		(67150)		
141	593	612	626	623	616	66		601sh	614sh	613sh	610sh	610sh	
				(59540)			**55**	–	605	615	–	610[a]	64
	567sh	578sh	585sh	579sh	573sh		**213**	588	608	631	632	616	172
29	537	566	605	–	577	66		565sh	584sh	598sh	600sh	561sh	
		(42780)					**214**	591	608	617	614	608	66
	516sh	591sh	584sh		602sh				(43740)		(44680)		
	565sh							564sh		581sh	576sh	576sh	
51	573	587	595	592	–	66	**58**	597	611	607	606	603	66
		(39540)						570sh					
	550sh	622sh	618sh	615sh			**215**	612	622	616	615	618	66
52	591	605	609	609	603	172			(65940)		(64480)		
	563sh	576sh	574sh	575sh	575sh			570sh	584	578sh	575sh	579sh	
209	607	618	623	623	615	172	**136**	603	617	609	607	612	66
	580sh	582sh	585sh	585sh	575sh				(59950)		(60650)		
170	617	633	638	632	633	66		574		572sh	571sh	574sh	
		(50760)		(50350)			**216**	556	568	608	604	601	66
	584sh	593sh	591sh	583sh	588sh				(42550)		(42600)		
210	624	635	641	635	637	172		581sh	595sh	571sh	573sh	561sh	
		(52700)		(51800)			**217**	593	609	617	618	612	66
	587sh		597sh	591sh	595sh				(58650)		(61800)		
174	618	632	639	636	633	172		568sh	578sh	580sh	579sh	575sh	
	589sh	593sh	597sh	594sh	590sh		**61**	612	620	607	606	612	172
53	596	612	626	622	617	66			(59870)		(57570)		
				(43840)				575sh	580sh	570sh	565sh	570sh	
	562sh	578sh	581sh	580sh	575sh		**66**	–	593	–	–	–	73
175	615	626	632	629	627	172	**67**	–	605	–	–	–	73
	583sh	585sh	588sh	588sh	590sh		**218**	556	594	597	599	597	172
211	632	645	642	641	641	66			(52680)		(57950)		
		(58780)		(60740)				577sh	563sh	561sh	558sh	559sh	
	567sh		604sh		600sh		**204**	568	582	598	598	589	172
172	658	668	658	657	657	172		543sh	552sh	573sh	573sh		
	615sh	625sh		611sh	618sh		**219**	–	585	–	–	–	174
77	543	567	592	593	572	66	**220**	–	604	–	–	–	174
		(56730)					**221**	–	592	–	–	–	174
	553sh	550sh	560sh	560sh	541sh		**103**	616[b]	–	654	–	634[a]	175
212	587	603	637	634	633	172		(63000)		(65000)		(70000)	
	624sh	637sh	606sh	601sh	596sh		**115**	–	584	593	592	588	96
133	623	638	642	640	638	66			(51610)	(56370)	(57700)	(55800)	
		(58600)		(58740)			**206**	–	588	597	596	592	96
	585sh	602sh	602sh	598sh	598sh				(52760)	(55470)	(56220)	(56360)	
132	631	645	643	642	643	66	**207**	588[b]	601	611	609	604	96
		(57520)		(60840)				(59690)	(60960)	(73300)	(72900)	(59100)	
	592sh	601sh	600sh	599sh	600sh		**208**	588[b]	601	611	609	604	96
								(61480)	(60670)	(78800)	(78150)	(61820)	

[a] Acetone as the solvent. [b] Heptane as the solvent.

aromatic nucleus. The shortest-wavelength absorption is observed for the merocyanine forms of azaindoline-containing SPO **45**–**47**. In particular, the spectrum of the form **B** of SPO **222** (6′-substituted derivative SPO **47**) in toluene has an absorption maximum at 478 nm.[20]



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The positions of the absorption maxima of the open forms of SPO depend on the polar properties of the solvents. The observed solvatochromic effect can be both positive and negative. In the case of spiroindolinonaphthooxazines, the sign of this effect is determined by the degree of quinoidation (or bipolarity) of the merocyanine form, which depends on the electron-donating and electron-withdrawing properties of the substituents and their positions in a particular moiety of SPO.[64,66]

Analysis of the dependence of the spectral characteristics of photomerocyanines **B** on empirical Brooker's parameters (χ_R and χ_B) of the solvents enables one to estimate their polar properties.[178–181] For 6′- and 8′-cyano-, 8′,9′-dicyano- and 8′-nitro-substituted spiroindolinonaphthooxazines, there is a correlation between the frequencies of the absorption maxima of the acyclic isomers **B** and the parameters χ_B, whereas a correlation with the parameters χ_R is lacking, which is indicative of the negative

solvatochromism.[66] The above-mentioned correlation is most pronounced in the presence of an additional substituent, *viz*., the methoxy group, at position 5. The observed effect provides evidence for a substantial charge delocalisation in the ground state of photomerocyanines resulting in stabilisation of the bipolar structure. By contrast, there is a correlation between the frequencies of the absorption maxima of the coloured forms **B** and the parameters χ_R for unsubstituted SPO **1** as well as for 6′-NC_5H_{10}-, 8′-OMe-, 9′-OMe- and 5-NO_2-substituted SPO, whereas there is no correlation with the parameters χ_B, *i.e*., these compounds exhibit the positive solvatochromism. This effect results from a weak polarity of the ground state of the acyclic isomer, *i.e*., from the predominantly quinoid structure of photomerocyanine **B**.

Hence, electron-withdrawing substituents in the naphthooxazine moiety of SPO would be expected to facilitate delocalisation of the negative charge on the oxygen atom giving rise to properties typical of bipolar structures. Electron-donating groups in the indoline fragment, which facilitate delocalisation of the positive charge on the nitrogen atom, exert an analogous effect. By contrast, a bipolar structure is thermodynamically unfavourable in the presence of electron-donating substituents in the naphthooxazine fragment, which facilitate an increase in the negative charge on the oxygen atom, and electron-withdrawing substituents in the indoline fragment, which lead to an increase in the positive charge on the nitrogen atom. As a consequence, the merocyanine form undergoes quinoidation. If substituents are present in both moieties of SPO, their effect would depend on which properties prevail.

There is a certain dependence of the changes in the intensities of long-wavelength absorption bands of the coloured forms of SPO on their molecular structures and properties of the solvents (see Table 8). The molar extinction coefficients of the absorption maxima of the merocyanine forms ($\varepsilon^{\mathbf{B}}_{max}$) are larger for the structures exhibiting bipolar properties than for the corresponding quinoid isomers. Thus, the $\varepsilon^{\mathbf{B}}_{max}$ coefficients for SPO **61**, **132**, **134**, **136**, **141**, **211** and **215** whose acyclic isomers have bipolar structures are in the range of 57 000 – 67 000 litre mol^{-1} cm^{-1}, whereas these coefficients for the quinoid forms **B** of SPO **1**, **33**, **56**, **214** and **216** are in the range of 40 000 – 45 000 litre mol^{-1} cm^{-1}.[66] An analogous effect is observed for indoline-containing SPO **115** and **206** – **208** of the phenanthroline series. The larger $\varepsilon^{\mathbf{B}}_{max}$ coefficients are observed for SPO **207** and **208** containing electron-donating (OAlk) substituents in the indoline moiety of SPO, which facilitate polarisation of the merocyanine form.[96] In polar solvents, the $\varepsilon^{\mathbf{B}}_{max}$ values for the absorption maxima of the coloured forms of SPO are generally larger than those in weakly polar solvents. The largest $\varepsilon^{\mathbf{B}}_{max}$ coefficients are observed for SPO **207** and **208** in alcohols. This is associated with the formation of intermolecular hydrogen bonds, which can stabilise bipolar forms of acyclic isomers.

VIII. Dark decolouration of spirooxazines

As mentioned above, the thermochromism of SPO is the temperature-induced change in the equilibrium between isomers in the ground electronic state. By analogy, the photochromism can be considered as the photoinduced change in the equilibrium giving rise to a new equilibrium between the isomers in which at least one isomer, for example, the cyclic isomer (in the general case, both **A** and **B** isomers), occurs in the excited state. The equilibrium position attained under continuous irradiation is known as the photostationary state. For a quantitative analysis of the system, it is important to establish the identity (or difference) of the products of thermal and photochemical transformations of the starting SPO. Generally, products of thermal and photochemical reactions of SPO observed in stationary conditions at temperatures higher than 10 °C are spectrally identical. After termination of irradiation, the system relaxes from the photostationary state to the thermal equilibrium state occurring at this temperature. This state

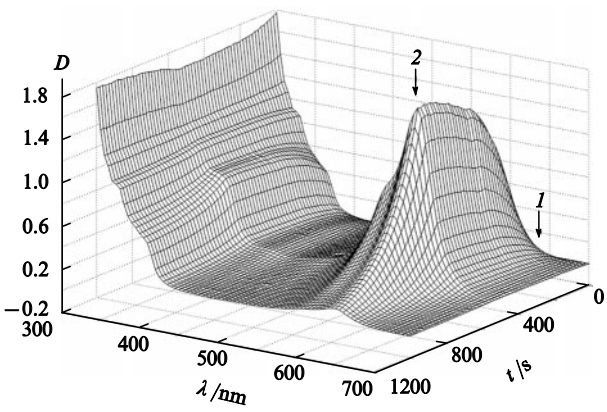


Figure 2. Evolution of the absorption spectra of SPO **58** in toluene ($c = 1.2 \times 10^{-4}$ mol litre^{-1}, $T = 293$ K) under irradiation with light at 365 nm (*1*) and after termination of irradiation (*2*).

is characterised by the rate constant, which is equal to the sum of the rate constants of the forward ($k_{\mathbf{AB}}$) and reverse thermal reactions ($k_{\mathbf{BA}}$) (Fig. 2). Since $k_{\mathbf{BA}} \gg k_{\mathbf{AB}}$ in most cases (*cf*. Tables 6 and 9), the observed relaxation process, which is referred to as a dark reaction and follows an exponential law in solutions, is described by the rate constant $k_{\mathbf{BA}}$. The value, which is inversely proportional to the apparent rate constant of dark decolouration, is often used in the discussion of the practical use of photochromes and referred to as the lifetime of the coloured form ($\tau_{\mathbf{B}}$). For solutions of SPO, $\tau_{\mathbf{B}}$ ranges from 10^{-1} to 10^4 s.

The characteristics of the dark decolouration reaction of SPO, *viz*., the rate constant ($k_{\mathbf{BA}}$) and the activation energy ($E_a^{\mathbf{BA}}$), vary over wide ranges depending on the molecular structure of SPO and the nature of the solvent (Table 9).

The solvents have an ambiguous effect on the rate constant of the reverse reaction of SPO, which is determined by the electron-donating and electron-withdrawing properties of substituents in the heterocyclic and oxazine fragments. In the case of spiroindolinonaphthooxazines, certain tendencies in the change of $k_{\mathbf{BA}}$ can be revealed. For monosubstituted compounds containing electron-donating substituent in the naphthooxazine fragment (for example, SPO **1**, **51**, **77**, **213**, **216**) or an electron-withdrawing substituent in the indoline fragment (SPO **29**), the rate constant increases in parallel with the polarity of the solvent. By contrast, the rate constant decreases with increasing polarity of the solvent for SPO containing electron-withdrawing groups in the indoline moiety (for example, SPO **58**, **132**, **133**, **136**, **213**) or electron-donating substituents in the naphthooxazine moiety (SPO **141**, **207**, **208**). If several substituents are present in both fragments of SPO, the direction in which the rate constant of the reverse reaction changes depending on the polar properties of the solvents is determined by the relation between the electron-donating and electron-withdrawing properties of the substituents in the indoline and naphthooxazine fragments. Therefore, the revealed correlations reflect to a certain extent the polarity of merocyanines. It should be noted that the rate constant of the reverse thermal reaction in solvents, which have specific interactions (such as alcohols) and can form intermolecular hydrogen bonds with photoinduced forms of SPO, can change stepwise rather than in parallel with the polar properties of the solvents, which are determined, for example, by the dielectric permeability (see Table 9).

In considering the effect of the molecular structure of SPO on the rate constant of the dark reaction, it is necessary to take into account the above-mentioned opposite relationships between the rate constant and the polar properties of the solvents. Nevertheless, there are general regularities, which persist regardless of the nature of the solvent. The introduction of electron-withdrawing substituents into the naphthooxazine moiety of spiroindoli-

Table 9. Characteristics of thermal recyclisation, *viz*., rate constants ($k_{\mathbf{BA}}$) and activation energies ($E_a^{\mathbf{BA}}$).

Compound	$10^{-2}k_{\mathbf{BA}}$ /s^{-1} ($E_a^{\mathbf{BA}}$ /kJ mol^{-1})					Ref.	Compound	$10^{-2}k_{\mathbf{BA}}$ /s^{-1} ($E_a^{\mathbf{BA}}$ /kJ mol^{-1})					Ref.
	cyclohexane	toluene	ethanol	methanol	acetonitrile			cyclohexane	toluene	ethanol	methanol	acetonitrile	
1	18.2 (68.4)	19.1 (62.8)	26.5 (85.9)	27.2 (83.3)	112.2 (86.1)	172	**132**	13.9 (70.6)	5.9 (97.0)	0.29 (93.6)	0.34 (86.2)	1.5 (94.2)	66
141	21.1 (67.8)	19.5 (66.8)	4.4 (94.2)	4.3 (94.3)	24.2 (88.8)	66	**134**	4.1 (86.5)	1.2 (95.3)	0.02 (99.5)	0.03 (96.1)	0.17 (99.8)	66
29	5.6 (64.5)	7.5 (80.0)	311.0	–	31.1 (67.1)	66	**213**	14.5 (77.0)	16.5 (69.2)	–	110.9 (85.0)	252.1 (61.5)	172
51	12.5 (71.6)	16.4 (77.5)	23.5 (83.0)	24.4 (80.1)	–	66	**214**	23.8 (71.0)	20.3 (67.0)	7.5 (91.4)	7.7 (90.3)	30.8 (81.1)	66
52	21.5 (72.3)	25.2 (72.2)	31.3 (78.2)	40.1 (82.8)	80.5 (67.7)	172	**58**	12.6 (77.8)	6.0 (88.1)	0.5 (99.1)	0.5 (97.0)	2.5 (95.9)	66
209	14.2 (68.1)	18.1 (82.1)	7.4 (96.2)	7.9 (93.7)	18.4 (87.5)	172	**215**	4.1 (86.3)	1.3 (94.0)	0.05 (105.7)	0.06 (103.5)	0.38 (97.8)	66
170	23.0 (71.4)	16.1 (83.7)	2.3 (90.0)	5.6 (72.1)	8.9 (88.3)	66	**136**	8.4 (80.0)	3.4 (93.5)	0.22 (99.7)	0.27 (97.0)	1.2 (95.3)	66
210	11.6 (77.5)	13.0 (84.5)	2.3 (88.8)	4.9 (72.8)	10.8 (86.8)	172	**216**	16.1 (77.5)	15.3 (69.0)	18.5 (88.7)	19.5 (85.2)	57.9 (73.6)	66
174	19.4 (72.1)	19.8 (79.7)	7.3 (87.4)	10.0 (84.3)	21.0 (90.4)	172	**217**	13.9 (73.0)	15.4 (63.8)	3.5 (95.5)	3.1 (94.4)	17.3 (71.5)	66
53	62.3 (70.5)	31.9 (72.9)	6.2 (83.5)	6.6 (89.5)	25.4 (84.0)	66	**61**	1.2 (69.2)	0.19 (99.0)	0.02 (94.4)	0.03 (91.6)	0.11 (97.8)	172
175	17.6 (76.7)	19.8 (78.3)	5.8 (92.0)	7.5 (92.5)	16.5 (88.8)	172	**218**[a]	21.4 (80.3)	16.7 (79.0)	–	1.4 (96.2)	17.5 (90.3)	172
211	14.7 (74.6)	5.9 (86.0)	1.0 (98.0)	1.1 (93.4)	3.0 (88.5)	66	**204**[a]	6.5 (73.6)	9.0 (73.3)	271.9 (56.3)	342.9 (46.4)	172.0 (77.4)	172
172	7.6 (79.0)	4.0 (88.7)	0.67 (92.4)	1.6 (77.7)	2.3 (92.3)	172	**115**[b]	–	16.3	11.5	11.7 (77.5)	58.3	96
77	3.6 (71.9)	4.7 (76.4)	275.0 (68.3)	410.7 (92.5)	45.1 (73.3)	66	**206**[b]	–	10.3	9.4	9.6 (78.5)	53.7	96
212	3.8 (75.4)	21.4 (67.5)	20.8 (76.6)	29.9 (78.8)	22.4 (86.4)	172	**207**[b]	9.8[c] (72.1)	12.9 (66.0)	1.9 (96.8)	1.7 (99.7)	8.4 (83.7)	96
133	28.3 (68.2)	7.8 (97.3)	0.32 (97.4)	0.37 (92.0)	1.9 (95.0)	66	**208**[b]	10.8[c] (76.6)	14.5 (70.5)	1.7 (100.3)	1.8 (114.0)	8.0 (83.9)	96

[a] For these SPO, $k_{\mathbf{BA}}$ and $E_a^{\mathbf{BA}}$ were determined at 298 K. [b] For SPO of the phenanthroline series, $k_{\mathbf{BA}}$ and $E_a^{\mathbf{BA}}$ were determined at 296 K. [c] Heptane as the solvent.

nonaphthooxazines leads to a decrease in the rate constant of the reverse thermal reaction, the simultaneous insertion of electron-donating groups at position 5 of the indoline fragment substantially enhancing this effect. The presence of electron-donating substituents at position 5 of the indoline fragment exerts an analogous effect in other spiroindolinooxazines, for example, in SPO of the phenanthroline series. The steric effect of bulky substituents on thermal decolouration of SPO is manifested in a decrease in the rate constant (*cf*., for example, SPO **170** and **210**, **115** and **206**, Table 9).

The temperature dependence of the rate constant of the dark reaction characterised by the activation energy has a tendency to be enhanced in polar solvents, particularly, in alcohols (see Table 9). Conceivably, a strengthening of intermolecular interactions between the alcohol molecules and merocyanine forms of SPO through hydrogen bonding leads to an increase in the activation barrier to the recyclisation reaction. There is no rather strict relationship between the activation barrier to the dark reaction and the molecular structure of SPO. However, it should be noted that spiroindolinonaphthooxazines containing electron-withdrawing substituents in the oxazine fragment are characterised by higher $E_a^{\mathbf{BA}}$ compared to the compounds with electron-donating substituents.

IX. Photochemical properties of spirooxazines

The efficiency of photoreactions is estimated from the quantum yields. However, the determination of the quantum yields for photochromic systems presents difficulties associated primarily with the determination of the molar extinction coefficients of the coloured forms. This is the reason why many researchers use more readily available parameters, such as the colourability [95] or photochromic response.[6]

In the general case, by the colourability is meant a certain value, which is either proportional or equal to the product of the quantum yield of the photoreaction (Φ_{col}) by the molar extinction coefficient at the absorption maximum of the photoproduct ($\varepsilon_{\mathbf{B}}$). For instance, the optical density at the induced absorption maximum measured directly after the flash of a photolytic lamp was taken as the colourability (A_0) in the study. [179] Since the energy of photolysing radiation remained stable in the course of the experiment, the authors of the cited study believed that it is reasonable to compare the efficiency of photoprocesses involving structurally similar photochromes in solutions with the same concentration.

In another study,[68] the colourability (A_∞) was assigned the equilibrium value of the optical density at the absorption maximum of the photoproducts formed in solutions of SPO with the same concentration in the photostationary state. Sometimes, ε_{app} {the apparent molar extinction coefficient numerically equal to the ratio $A_0/([A]l)$, where [A] is the initial concentration of the

photochrome and l is the optical path length} is used instead of A_0.[180]

The photochromic responses for several groups of SPO were given in the review.[6] The authors noted that an estimating comparison of the efficiency of photocolouration of photochromes belonging to the same group of SPO can be performed, whereas a comparison of photochromes belonging to different groups is impermissible. A more strict approach to the estimation of the efficiency of photoreactions was proposed in the study.[181] In the cited study, the product $\Phi_{col}\varepsilon_{\mathbf{B}}$ was determined taking into account the fraction of light absorbed by the initial form. In this case, the colourability is independent of the conditions of irradiation. However, the uncertainty in the estimation of the photochemical activity of molecular systems associated with the determination of $\varepsilon_{\mathbf{B}}$ persists.

The universal character of the quantum yields (unlike the colourability) enables one to compare the photochemical properties of compounds with different structures in various media and in a wide temperature range. The correctness of the determination of the quantum yields of phototransformations depends on how much the molar extinction coefficients of the coloured forms determined by a particular method differ from the true values.

One method for the determination of the molar extinction coefficients, which is based on stabilisation and accumulation of photoproducts, involves the photocolouration reaction at low temperatures excluding the reverse ¶ thermal reaction.[13, 166, 175, 182] It is assumed that low-temperature photolysis affords only one stable isomer of the coloured form.

In alternative methods for the determination of the molar extinction coefficients, the coloured form is stabilised by the reactions with acids (protonation) or metal ions (complex formation). Actually, the starting form is completely consumed in these reactions, *i.e.*, the complete conversion $\mathbf{A} \rightarrow \mathbf{B}$ takes place. However, the resulting compounds have spectral characteristics, which differ from those of the photoproducts, and the assumption that their molar extinction coefficients have similar values seems to be unjustified.

A method for the determination of the molar extinction coefficients of the coloured forms with the use of the quantitative analysis of the equilibrium $\mathbf{A} \rightleftarrows \mathbf{B}$ by NMR spectroscopy and spectrophotometry is quite rigorous, but the application of this method is limited to a narrow range of compounds for which the content of the coloured form in the equilibrium mixture is sufficient for NMR spectroscopic study.[95, 96]

Good results were obtained with the use of a photokinetic method by analysing the kinetic curves, which are measured under continuous irradiation.[183] However, this method places stringent requirements on the planning and execution of the experiment as well as on the accuracy of the determination of the initial parameters (initial concentration of the photochromic compound, intensity of incident light, temperature, *etc.*). Thermal and photochemical processes, which occur in the systems within the framework of the assumed model, are described by a differential equation system including the molar extinction coefficients of the initial forms and final products, quantum yields of forward and reverse photoreactions and rate constants of thermal processes. A solution of this differential equation system enables one to obtain model characteristics of photochromic systems. However, even in the simplest case, the model includes four processes (forward and reverse thermal and photochemical reactions) involving two forms of SPO (initial cyclic and merocyanine) and, hence, the differential equation system cannot be solved analytically. To solve such systems, researchers have to use various approximations, in which particular processes are ignored.

¶ The occurrence of the reverse photoreaction leads to the attainment of a photostationary state rather than to the complete conversion $\mathbf{A} \rightarrow \mathbf{B}$ and, as a consequence, to the error in the determination of the molar extinction coefficients.

For example, in one of the first studies[184] devoted to the detailed investigation of the kinetics of photoinduced processes in SPO molecules, the authors considered spiroindolinonaphthooxazines containing electron-donating substituents at position 6′ and concluded that the reverse photoreaction could be ignored because the ratio of the quantum yields of the reverse and forward photoreactions is in the range of 0.03–0.07. In more recent studies[166, 168, 185] of the kinetics of photoinduced reactions of SPO, whose molecular structures differ from those studied earlier, the authors also ignored the reverse photoreaction with the unjustified reference to the results of the study.[184]

An approach which involves the numerical integration of differential equations using the Runge–Kutta method and an iteration procedure using the Powell minimisation algorithm shows more promise. In this approach, the calculated and experimental photokinetic curves are compared and the modification of the parameters of the photochromic system is terminated once the discrepancy between the curves reaches the specified minimum value. The results obtained with the use of this method (in particular, for SPO)[66, 96] are characterised by high stability and are independent of a particular experimental apparatus.

The quantum yields of photocolouration ($\Phi_{\mathbf{AB}}$) of SPO are higher than those of photodecolouration ($\Phi_{\mathbf{BA}}$), but the differences do not always reach the value given in the study.[184] As can be seen from Table 10, the quantum yield ratio $\Phi_{\mathbf{BA}}/\Phi_{\mathbf{AB}}$ varies from 0.001 to 0.5 depending on the structure of SPO and the nature of the solvents.

The efficiency of the forward photoreaction decreases in the presence of electron-withdrawing substituents in the naphthooxazine fragment and, by contrast, the presence of electron-donating groups in this moiety of SPO does not lead to changes (or increases) in the yields of the coloured isomers compared to unsubstituted SPO **1**. The introduction of electron-donating groups at position 5 of the indoline fragment leads to a noticeable decrease in the quantum yield of the forward photoreaction.

The quantum yields of photodecolouration upon the above-mentioned structural modifications are changed in the opposite order. For SPO containing electron-withdrawing substituents in the naphthooxazine fragment, $\Phi_{\mathbf{BA}}$ are higher than those for SPO containing electron-donating substituents. In most cases, the introduction of the alkoxy groups at position 5 of the indoline fragment facilitates photorecyclisation.

The dependences of the quantum yields of the forward and reverse photoreactions of SPO on the nature of the solvent are opposite in character, *i.e.*, the quantum yields of photocolouration are lower in polar solvents and alcohols, whereas the efficiency of photodecolouration is lower in non-polar solvents (see Table 10).

The influence of the molecular structure and properties of the solvents on the efficiency of photoprocesses in SPO molecules correlates with their effect on the activation energy of thermal recyclisation because of the characteristic features of the structural and energy mechanisms of photoinduced reactions in SPO molecules.

The formation of the coloured product proceeds in two steps involving the $C_{spiro}-O$ bond cleavage followed by *cis–trans* isomerisation to the stable merocyanine form. Picosecond[188–190] and femtosecond[191, 192] photolysis revealed the existence of a short-lived cisoid[190] intermediate generated in the course of the $\mathbf{A} \rightarrow \mathbf{B}$ transformation. In these studies, an important conclusion concerning the energy mechanism of SPO photocolouration was made. It was established that only singlet excited states are involved in the photoinduced transformations of SPO.

The excitation of SPO molecules to the S_1 state is accompanied by the adiabatic $C_{spiro}-O$ bond cleavage and the formation of the cisoid isomer of the merocyanine form, which is then transformed into the ground state. Isomerisation gives rise to the metastable *TTC* isomer. This accounts for the fact that an increase in the potential barrier $E_a^{\mathbf{AB}}$ can lead to a decrease in the observed yield of the coloured product **B**. For the reverse photoreaction

Table 10. Quantum yields of photocolouration (Φ_{AB}) and photodecolouration (Φ_{BA}) of spirooxazines.

Compound	Solvent	Φ_{AB}	Φ_{BA}	Ref.	Compound	Solvent	Φ_{AB}	Φ_{BA}	Ref.
1	toluene	0.23	–	184	**215**	toluene	0.14	0.017	66
	"	0.22	–	186		methanol	0.09	0.037	66
	methylcyclohexane	0.41	–	168, 185	**136**	toluene	0.58	0.014	66
	ethanol	0.32	–	168, 185		"	0.70	–	187
	methanol	0.19	–	186		methanol	0.35	0.037	66
201	methylcyclohexane	0.46	–	168		methylcyclohexane	1.10	–	168
	ethanol	0.42	–	168		ethanol	0.72	–	168
165	methylcyclohexane	0.25	–	185	**216**	toluene	0.36	0.012	66
	ethanol	0.18	–	185		methanol	0.35	0.013	66
141	methanol	0.13	0.025	66	**217**	toluene	0.14	0.012	66
29	toluene	0.62	0.016	66		methanol	0.11	0.027	66
51	"	0.38	0.001	66	**61**	toluene	0.16	0.029	172
170	"	0.35	0.007	66		methanol	0.08	0.046	172
	methanol	0.13	0.023	66	**218**	toluene	0.19	0.011	172
210	toluene	0.34	0.009	172		"	0.14	–	186
	methanol	0.12	0.023	172		methanol	0.15	0.026	172
53	"	0.13	0.019	66		"	0.10	–	186
211	toluene	0.12	0.009	66	**204**	methylcyclohexane	0.49	–	168, 185
	methanol	0.06	0.019	66		ethanol	0.29	–	168, 185
77	toluene	0.48	0.004	66	**205**	methylcyclohexane	0.51	–	168
	"	0.50	–	187		ethanol	0.85	–	168
	"	0.42	–	184	**115**	toluene	0.26	0.005	96
	methylcyclohexane	0.55	–	185		ethanol	0.24	0.016	96
	ethanol	0.65	–	185		methanol	0.24	0.022	96
78	toluene	0.50	–	187		acetonitrile	0.26	0.011	96
82	"	0.20	–	184	**206**	toluene	0.25	0.002	96
133	"	0.20	0.009	66		ethanol	0.25	0.012	96
	methanol	0.12	0.029	66		methanol	0.24	0.015	96
132	toluene	0.17	0.011	66		acetonitrile	0.16	0.014	96
	methanol	0.11	0.027	66	**207**	heptane	0.12	0.003	96
134	toluene	0.11	0.016	66		toluene	0.15	0.003	96
	methanol	0.05	0.024	66		ethanol	0.09	0.025	96
214	toluene	0.32	0.018	66		methanol	0.09	0.032	96
	methanol	0.28	0.031	66		acetonitrile	0.12	0.019	96
202	methylcyclohexane	0.35	–	168, 185	**208**	heptane	0.14	0.003	96
	ethanol	0.36	–	168, 185		toluene	0.18	0.002	96
203	methylcyclohexane	0.14	–	168		ethanol	0.11	0.026	96
	ethanol	0.23	–	168		methanol	0.09	0.030	96
						acetonitrile	0.11	0.019	96

(assuming that it proceeds through the same cisoid intermediate), an increase in the barrier E_a^{BA} leads to an increase in probability of recyclisation.

Apparently, high quantum yields of photocolouration of nitro-substituted spiroindolinonaphthooxazines are associated with the triplet reaction mechanism.[187] This assumption is indirectly supported by low photostability of 5-nitro-substituted spiroindolinonaphthooxazine **29**.[193]

The resistance of photochromes to photodegradation depends also on the involvement of the triplet states of the starting, intermediate and final forms in phototransformations of the photochromes because the molecules in the triplet state possess higher reactivity and can interact with dissolved oxygen and solvent molecules as well as can undergo irreversible intramolecular rearrangements. The degrees of photodegradation of SPO are lower than those of their structural analogues, *viz*., spiropyrans,[193] which is in good agreement with the singlet mechanism of phototransformations found for a series of SPO.

Destruction of spirooxazines was considered in the review.[116]

X. Conclusion

On the basis of the above-considered published data, it can be stated that a qualitative and quantitative leap forward has been made in the chemistry of SPO. Particularly considerable progress has been achieved in the synthesis and functionalisation of spirooxazines. Numerous investigations revealed the structural factors, which exert an effect on the spectral characteristics, thermodynamic parameters of equilibria, kinetics of relaxation processes and efficiency of SPO phototransformations.

Due to the preparation of a large number of new SPO, the field of their practical application has been substantially extended. In particular, the possibilities of the use of spirooxazines in materials for recording information, optical switches [194] and photochromic chemosensors [195, 196] were considered.

However, a series of practically important properties of spirooxazines are as yet insufficiently known, which leaves a wide sphere of research activity. In particular, photochromic processes in the solid phase were poorly studied.[124, 197] Data on the fluorescence properties of spirooxazines are scarce.[198] Data on cross-sections of two-photon light absorption of cyclic and merocyanine forms of SPO are lacking. The latter parameter is of importance in using SPO for the construction of media for the three-dimensional recording systems (molecular memory) and photomodulated biomaterials. For spiropyrans, this parameter reaches 10^{-48} cm^4 s (which is a large value for organic molecules; see Ref. 199). For structurally similar spirooxazines, this parameter would be expected to assume values of the same order of magnitude. Finally, there are only scarce data on the supramolecular effects exhibited by spirooxazines. The first evidence [200]

for the formation of stable aggregates of merocyanine forms in solutions of spirooxazines, which are characterised by narrow absorption bands and are of interest for multifrequency systems,[201] have been published only recently.

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