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The Photochemistry and Photophysics of Spiropyrans

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The results of studies on the structure and nature of the electronic states of spiropyrans (SP) and the products of their photochromic reactions as well as the mechanism of the dissociation of the C_{spiro}-O bond and the formation of a coloured form of the SP are surveyed and analysed. Also analysed are the mechanisms of the α-dissociation and predissociation of the bond, which make it possible to explain satisfactorily the dependence of the quantum yield of the photocolouring reaction on the structure of the SP, the nature of the matrix, and temperature. The prospects for the utilisation of the photochromic SP are discussed.
The bibliography includes 179 references.

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I. INTRODUCTION

The photochromic spiropyrans (SP) have continuously attracted the attention of investigators. By virtue of their unique properties, they have been finding increasing applications. This is also promoted by the fact that the photochromic properties of SP are manifested in virtually any matrix—in the pure compound (in the crystalline or amorphous state), in solutions, and in polymers, and the conditions under which these matrices exist can vary over a wide range of temperature, viscosity, external pressure, and electric and magnetic field strengths. This makes it possible to employ SP as test objects in the study of the properties of the medium and of the mechanisms of its influence on the intramolecular photophysical and photochemical processes.

Spiropyrans are already used to prepare reusable polymeric photochromic materials or variable density light filters,[1-9] but their application for these purposes is limited by the low light sensitivity of the photomaterials and because enough cyclic information recording and deletion processes cannot be achieved. Apparently in the future SP will also be applied in other equally important fields. For example, it has been reported that they can be used as photoregulators of the ionic conductivity of membranes,[10] as modulators of the intensity of the fluorescence of monolayers,[11,12] etc. Presumably in the near future they will be used as elements in electronic circuits acting at the molecular level.[13,14]

Since the publication of the authors' earlier review,[15] numerous communications concerning the study of the photochromic reactions of SP and their structure have appeared. The fairly large amount of the data which have accumulated and, what is most important, its significance for the understanding of the photochemistry and photophysics of SP urgently require a critical analysis and a survey of the entire set of the results available.

As before,[15] in the analysis of the results of the studies of the primary photochemical processes as a function of the structure of the SP and external conditions, the SP are regarded as representatives of a specific class of organic compounds containing heteroatoms and belonging to the $(\sigma\pi nl)$ type in terms of the orbital classification of electronic states.[16-19]

Analysis of the experimental results has shown that the photochemical activity of SP and their luminescence characteristics are determined by the position of the energy levels and the orbital nature of the lowest electronically excited states. Furthermore, in order to understand the mechanism of the photodissociation of the bond in SP, it is essential to take into account the degree of involvement of the electrons of the heteroatoms in the configuration of the electronically excited states and also the interaction of the electronic orbitals of the mutually orthogonal heterocycles in both ground and excited states.

The SP photocolouring reaction can be represented schematically as follows in a general form:[6,15]

$$A \underset{}{\overset{h\nu}{\rightleftarrows}} A^* \overset{\varphi_d}{\rightarrow} X \overset{\varphi}{\rightarrow} B, \qquad (1)$$

where A is the colourless initial spiro-form of the SP, A^* its electronically excited state, X the *cis*-cisoid isomer of the coloured form arising after the dissociation of the bond and still preserving the orthogonality of the heterocycles, B the planar coloured form of the SP, ϕ the quantum yield in the formation reaction of the B form, and ϕ_d the quantum yield in the bond dissociation process. The recombination reactions of the photoproducts with transition to the initial state and also the possible pathway leading to the formation of the B form without the formation of the intermediate X isomer are not shown in Scheme (1).

The chemical structure of the SP considered in the review are presented in Tables 1 and 2. Table 1 also lists the known quantum yields of the SP colouring reaction under the influence of light with λ = 313 and 365 nm (ϕ_{313} and ϕ_{365} respectively). The yields ϕ were determined in weakly polar solvents at temperatures close to room temperature. The total number of SP investigated for which the values of ϕ are known is much greater;[6,9,15,20-35] Table 1 includes only some SP with characteristic structures and substituents. The yields ϕ in different matrices (for certain SP) are presented in Table 3.

II. THE NATURE OF THE ELECTRONIC STATES OF SPIROPYRANS AND THE PRODUCTS OF THEIR PHOTOCHROMIC REACTIONS

1. The Structure of Spiropyrans and Their Photoproducts

The structures of more than ten SP, including the strucures of the coloured forms,[38] have now been investigated y X-ray diffraction (XD).[36–41] The XD data show that n almost all the SP investigated the angle between the heterocycles is 90°. However, the heterocycles themselves are non-planar—the angle of the bend in the planes of the indoline ring system along the C(3)–N(1) line is 23–30° and the angle in the bend in the benzopyran ring system along the C(3′)–O(1′) line is 11–17°,[38] depending on the ring substituents.

Table 1. The structure of spiropyrans and the quantum yields of the photocolouring reactions.

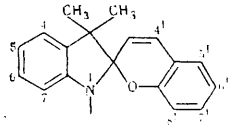
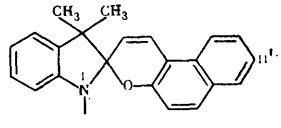
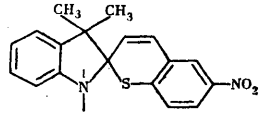
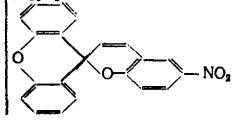
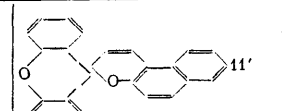
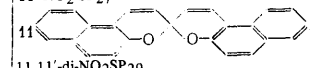
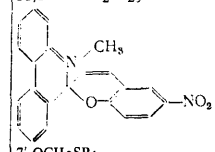
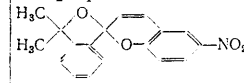
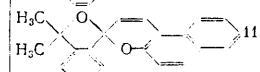
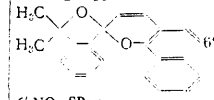
SP	Structure of SP and substituents	Solvent	φ_{313}	φ_{365}	Refs.
					
SP_1	1-CH_3	hx, t	0.1	—	[6, 15]
SP_2	1-CH_3-6′-Br	t	0.03	—	[22]
SP_3	1-CH_3-6′-NO_2	t	—	0.76	[20, 21]
,,	»	ea	0.40	0.60	[20, 21]
SP_4	1-CH_3-6′-NO_2-8′-OCH_3	t	—	0.59	[21, 23]
,,	»	d, ea	0.30	0.45	[6, 15]
SP_5	1-C_6H_5-6′-NO_2-8′-OCH_3	ea	0.10	0.45	[15, 26]
SP_6	1-CH_3-6′-NO_2-8′-C_3H_5	ea	—	0.55	[26]
SP_7	1-C_6H_5-6′-NO_2-8′-Br	ea	—	0.45	[26]
SP_8	1-C_6H_5-8′-NO_2	ea	—	0.13	[26]
SP_9	1-CH_3-6′-Cl-8′-NO_2	ea	—	0.05	[26]
SP_{10}	1-CH_3-4,5-benzo-6′-NO_2	ea	—	0.025	[26]
SP_{11}	1-CH_3-5-NO_2	hp	—	0.56	[21, 25]
SP_{12}	1-CH_3-5-NO_2-6′-OCH_3	hp	—	0.60	[21, 25]
,,	»	t	0.36	0.60	[21, 25]
,,	»	ea	—	0.33	[21, 25]
SP_{13}	1-CH_3-5′,7′-dichloro-6′-NO_2	d	0.47	0.58	[6]
,,	»	t	0.45	0.55	[6]
SP_{14}	1-CH_3-6′-NO_2-8′-Br	–	—	—	—
SP_{15}	1-CH_3-5-CH_3CO-6′-NO_2-8′-OCH_3	t	—	0.24	[9]
SP_{16}	1-C_2H_4OH-6′-NO_2	–	—	—	—
SP_{17}	1-C_2H_4-O-CO-C_3H_5-6′-NO_2	–	—	—	—
SP_{18}	1-$C_{18}H_{35}$-6′-NO_2	–	—	0.45	[11]
SP_{19}	1-C_4H_9-6′-NO_2	–	—	—	—
SP_{20}	1-C_2H_4-2-O-CO-$CH(CH_3)_2$-NO_2	–	—	—	—
					
SP_{21}	1-CH_3	t	0.07	0.27	[22]
,,	»	mch	0.06	—	[6]
SP_{22}	1-CH_3-11′-NO_2	t	—	0.60	[27]
SP_{23}	1-C_6H_5-11′-NO_2	t	—	0.08	[27]
					
SP_{24}	1-CH_3	t	—	~0.2	[34]
SP_{25}	1-C_6H_5	t	—	~0.3	[34]
SP_{26}		t	—	≤0.1	[21]

Table 1 (contd.).

SP	Structure of SP and substituents	Solvent	φ_{313}	φ_{365}	Refs.
SP_{27}		t	0.45	0.45	[22]
SP_{28}	11′-NO_2-SP_{27}	t	—	0.08	[27]
SP_{29}		t	0.55	0.07	[22]
SP_{30}	11,11′-di-NO_2SP_{29}	d	—	0.59	[6]
SP_{31}		t	—	0.03	[31]
SP_{32}	7′-OCH_3SP_1	t	0.03	—	[35]
SP_{33}	7′-NO_2-SP_1	ea	—	0.17	[26]
SP_{34}		tip	0.30	0.25	[33]
SP_{35}		tip	0.60	0.03	[33]
SP_{36}	11′-NO_2-SP_{35}	tip	—	0.40	[33]
SP_{37}		tip	0.55	0.12	[33]
SP_{38}	6′-NO_2-SP_{37}	tip	—	0.40	[33]

Notation: t = toluene, d = dioxan, ea = ethyl acetate, hx = hexane, mch = methylcyclohexane, hp = heptane, and tip = t : 1 toluene–isopentane mixture.

Table 2. The lengths of the dissociating bonds (r) in spiropyrans and the activation energies (E_a^*) for the thermal bond dissociation reaction.

SP	r, Å	E_a^*, kcal mol^{-1}	Refs.
SP_1	—	10	[35]
SP_2	—	9.3	[35]
SP_3	1.486	12	[35, 39]
SP_8	1.492	7.6	[35, 36]
SP_9	1.497	8.5	[35, 37]
SP_{11}	1.453	13	[35, 38]
SP_{14}	1.495	—	[38]
SP_{21}	—	7.8	[35]
SP_{22}	—	8.0	[35]
SP_{23}	1.462	9.4	[35, 38]
SP_{25}	1.487	—	[40]
SP_{27}	—	7.4	[35]
SP_{32}	1.471	6.1	[35, 38]
SP_{33}	—	6.0	[35]
SP_{34}	1.454	15	[35, 41]
SP_{35}, SP_{36}	—	8.1	[35]
SP_{37}	1.444	—	[38]
SP_{38}	1.465	—	[38]

*The activation energies E_a were determined in a matrix comprising the given compound—the melt or the amorphous vitreous state of the SP.

It is of interest to compare the length of the dissociating bond r with the activation energies E_a for the thermal bond dissociation in SP and the quantum yield in the photocolouring reaction (Tables 1 and 2). The values of E_a for all

SP with the exception of SP_{32} and SP_{33} are correlated with r: as a rule, E_a falls with increase of r. The introduction of substituents in the 7′-position stabilises the coloured form of the SP as well as the E_a as a result of the conjugation of the substituent orbitals with the π orbital of the central carbon atom.[7,35,38] The correlation between E_a and r is a consequence of the fact that the dissociation of the bond in the thermal reaction proceeds via the ground electronic state of the vibrationally excited SP.

Table 3. The quantum yields ϕ_{365} for spiropyrans in various media*.

Medium**	SP					
	SP_3	SP_{12}	SP_{13}	SP_{21}	SP_{22}	SP_{27}
Toluene (2.38)	0.76	0.60	0.55	0.27	0.60	0.45
Dioxan	—	—	0.58	—	—	—
CCl_4	0.73	—	—	—	—	—
Ethyl acetate (6.02)	0.60	0.33	—	—	—	—
1-Propanol (20.1)	0.14	0.06	—	—	—	—
Ethanol (24.3)	0.12; 0.01 (77 K)	—	0.31	0.30	0.05	0.5
Acetonitrile (36.2)	0.06	0.05	0.107; 0.43***	—	—	—
Dimethylformamide (36.7)	0.10	0.08	—	0.2	—	—
Polystyrene	0.7; 0.1 (77 K)	0	—	0.02 (77 K)	0.3	0.2 (77 K)
Poly(methyl methacrylate)	0.31; 0.07 (77 K)	0	—	—	—	—

*With the exception of specially noted cases, the temperature was close to room temperature. The yields ϕ_{365} were taken from Bertelson[6] for SP_{13}, from Reeves and Wilkinson[29] for SP_3 in PMMA at room temperature, and from Kholmanskii[22] and Kholmanskii and Tarasov[24] in the remaining cases.
**The dielectric constant ε is indicated in brackets.
***The quantum yield of the sensitised colouring reaction.

On the other hand, there is no correlation between ϕ and r. This shows in its turn that the photodissociation of the bond in the SP proceeds via the electronically excited state of the SP whose orbital nature determines the mechanism and the quantum yield ϕ of the SP photocolouring reaction. Therefore, in predicting the photochemical activity of the SP from XD data, it is essential to take into account the factors which can affect the orbital nature of the excited state, the intensity of the electronic transition, and also the effectiveness of the interaction of the electrons of various heterocycles in the excited state. Such factors are in the first place the orientation of the nitro-group relative to the plane of the benzene ring and other substituents, and the spatial orientation of the l orbitals of the heteroatom and the dissociating bond as well as the heterocycles themselves.

Since the pyran ring in the SP is nearly planar and the C–O–C angle is 119°,[36–38] presumably the valence orbitals of the oxygen heteroatom are sp^2-hybridised.

In the indoline ring of the SP, the nitrogen atom is somewhat displaced out of the plane drawn through the carbon atoms linked to it (in particular by 0.26 Å for SP_{11} [38]). The valence angles between the N–C bonds in SP_{11} are 121.4°, 119.9°, and 108.8°.[38] These data suggest the sp^2-hybridisation also of the atomic orbitals of nitrogen, although it is somewhat distorted by virtue of steric factors. This is also indicated by the comparison of the structural and luminescence-spectroscopic characteristics of SP and aromatic amines in which the nitrogen atom is sp^2-hybridised.[42]

Indeed the values λ_{max} = 375 nm and $\varepsilon_{375} = 1.8 \times 10^4$ litre mol^{-1} cm^{-1} [21,25] for the first absorption band in the spectrum of the SP having the nitro-group in the indoline ring (SP_{11}) are virtually identical with the corresponding values for *p*-nitroaniline and *NN*-dimethyl-*p*-nitroaniline (376 nm and 1.6×10^4 litre mol^{-1} cm^{-1} for the former and 388 nm and 1.8×10^4 litre mol^{-1} cm^{-1} for the latter[43]). We may note that the agreement between the spectra and phosphorescence decay times for SP_{11} and nitroaniline[44] also indicates the similarity of the electronic structures of the T_1 states of these compounds.

In order to determine the structure of the coloured form of the SP, IR spectroscopic,[7,45] Raman spectroscopic,[46] and photoelectron spectroscopic[47] methods were resorted to in addition to XD. Studies,[9,48–58] including, for example, polarisation measurements,[51–54] measurements of the dipole moments of the coloured molecules,[56,57] and quantum-chemical calculations,[58] have also been devoted to the investigation of the structure and properties of the coloured form and its isomers.

2. Luminescence-Spectroscopic Characteristics of Spiropyrans

The study of the orbital nature of the electronically excited states had as its primary aim the elucidation of the degree of involvement of the electrons of the heteroatoms in the electronic configuration of the lowest excited states of the ππ* type. The orbital nature of the lowest electronically excited states of SP and their energy are determined by investigating the absorption and luminescence spectra using the theory of solvatochromism.[59,60] Methods based on quantum-chemical calculations for SP or compounds modelling their fragments have also been resorted to in order to achieve a qualitative justification.[8,58,61–63] With the aid of these calculations and the theory of solvatochromism, the charges on the heteroatoms in the excited states were estimated. For this purpose, a study was also made of the deactivation of the triplet photochemically active (PCA) state of the SP by various quenching agents and in the first place by electron donors. The optical absorption spectra of certain characteristic SP have been published.[5,21,22,26,27,64–69]

The electronic transition of the π–π* type in SP without the nitro-group can be represented as a linear combination of one electron π–π* (in the aromatic system) and *l*–π* (electron transition from the heteroatom to the π* orbital of the aromatic system) transitions and can be designated by *πl*–π*.[15,18,19]

Calculations have been made for the electronic transitions and the distribution of the electron density in the S_0, S_1, and T_1 states of SP_1 has been evaluated by the CNDO method.[61] The calculated transition energies as well as the assignment of the first transition in the benzopyran ring to the π–π* type agree qualitatively with experimental data. The redistribution of electron density in the S_1 and T_1 states leads to the appearance of a positive charge on the oxygen (0.07), nitrogen (0.03), and spiro-carbon (0.017) atoms relative to the S_0 state. These results agree with the assignment of the lowest S_1 and T_2 states to the (*πl*, π*) type or, briefly, the *L* type.

On the basis of the results of theoretical calculations,[8,61,63] one can assume that the positive charge on the heteroatom of SP_1 in the S_1 and T_1 states is ~0.1. We may note that the contribution of the (*l*, π*) configuration to the excited state of the molecule is determined by the charge on the heteroatom.[63]

The introduction of an electron-donating substituent into the SP heterocycle leads to the appearance of an additional absorption band due to the transition involving charge transfer (CT) from the electron-donating substituent to the π^* orbital of the π-electron system.[22] The contribution of the (l, π^*) configuration then diminishes and the positive charge on the oxygen heteroatom in the excited state is reduced as a result compared with the corresponding value for SP_1.[23,55]

The first transition in unsubstituted SP with the naphthopyran ring (SP_{21}, SP_{27}, and SP_{29}) is also of the $\pi l-\pi^*$ type;[22] this has been confirmed by solvatochromic studies and the presence in the absorption spectrum of bands due to stretching (1290–1350 cm^{-1}) and deformation (450–500 cm^{-1}) vibrations of the COC group.[22,64,65]

Since it is known from theoretical calculations[18,19,63] that the contribution of the (l, π^*) configuration to the excited state falls as the π-conjugation chain lengthens, presumably in the case of SP with the naphthopyran ring the positive charge on the oxygen heteroatom is smaller than for SP_1.

The introduction of a nitro-group into any of the SP fragments results in the appearance of a low-energy $\pi-\pi^*$ transition, which involves intramolecular charge transfer.[15,21,26,27,30,48,66–69] A spiropyran with the nitro-group in the benzopyran ring (A) can be designated by DSA, where D represents a heterocycle with a fairly low ionisation potential I (indoline, xanthene, benzothiazole, etc.) and C represents the spiro-carbon atom. It is known[70] that in molecules of the DSA type in which the D and A fragments are separated by three σ-bonds, apart from the local $\pi-\pi^*$ transition in the A fragment, hyperconjugation via the system of σ-bonds is responsible for the charge-transfer transition from the D to the A fragment:

$$DSA \xrightarrow{h\nu} (D^+SA^-)^*. \qquad (2)$$

The positions and intensities of the absorption bands corresponding to the transitions in the A fragment and in process (2) are determined by the value of I for the D fragment and the electron affinity ε_A for the A fragment as well as the energy of the interaction of the (DSA*) and $(D^+SA^-)^*$ configurations.[70]

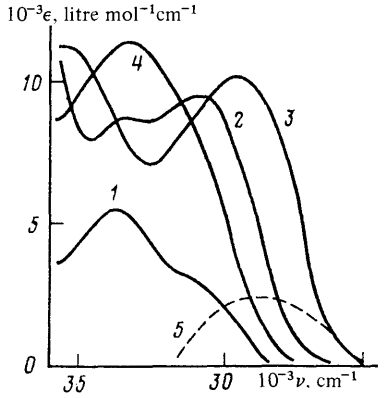


Figure 1. Absorption spectra of SP in isopentane: 1) SP_1; 2) SP_3; 3) SP_4; 4) SP_{34}; 5) difference between the absorption spectra of SP_4 and 8-methoxy-6-nitro-2*H*-chromene (MA).[68]

In SP the interaction with the π electrons of the D and A rings as a consequence of spiroconjugation[62] and the hyperconjugation of the n, σ, and π orbitals of the non-planar D and A rings in the ground state of the spiropyran can also lead to the appearance of a transition of type (2).[61]

Indeed comparison of the absorption spectra of SP having different D rings with the spectrum of the molecule modelling the A ring (MA), presented in two publications,[68,69] makes it possible to discover in the spectrum of the SP an additional absorption band whose position (ν_M^{DA}) depends on the structure of the D ring and which has an extinction coefficient ε a factor of 2–3 smaller than the band due to the transition in the A ring. The value of ν_M^{DA} for indoline SP is close to ν_M^A for the band due to the $\pi-\pi^*$ transition with charge transfer in the A ring, which is designated by $\pi l-\pi^*\pi_n^*$,[15,16,21,26] where π_n^* represents the orbital of the nitro-group and l the orbital of the heteroatom conjugated with the π system of the benzene ring[42] (Fig. 1). The first absorption band in the spectra of these SP therefore constitutes a superposition of the absorption band due to the charge transfer transition in the A ring and the transition (2). Since I for the D ring in SP_{34} is greater than I for the D ring in SP_3,[70] the frequency ν_M^{DA} for SP_{34} should be greater than for SP_3. It is therefore evident that ν_M for the first absorption band of SP_{34} is greater than ν_M for SP_3 (Fig. 1).

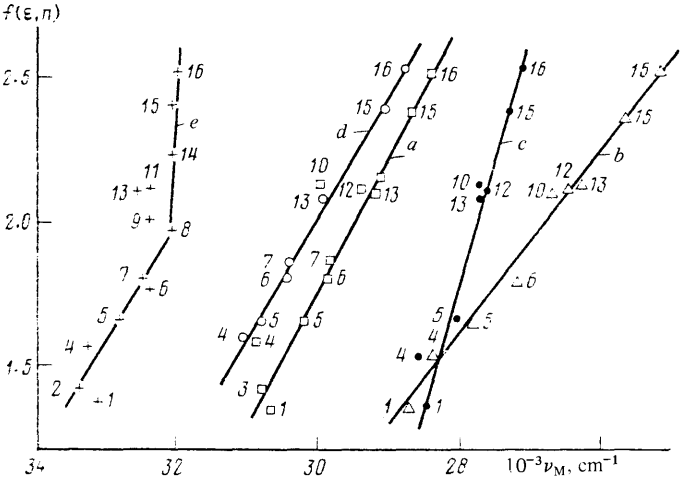


Figure 2. Dependence of the positions of the maxima of the first absorption bands of SP_3 (*a*), SP_{11} (*b*), SP_{24} (*c*), SP_{26} (*d*), and SP_{34} (*e*) on the universal interaction function $f(\varepsilon, n)$: 1) hexane; 2) isopentane; 3) cyclohexane; 4) heptane; 5) carbon tetrachloride; 6) benzene; 7) toluene; 8) chloroform; 9) tetrahydrofuran; 10) ethanol; 11) methanol; 12) acetone; 13) acetonitrile; 14) chlorobenzene; 15) dimethylformamide; 16) dimethyl sulphoxide.[66,67]

The energies of the (π, π^*) states (DSA*) and $(D^+SA^-)^*$ of spiropyran diminish as a result of general interaction with the solvent and to a greater extent than the energy of the ground state of SP.[59,60] If the molecule has no isolated orbitals, the dependence of ν_M on the dielectric constant and the refractive index is described in this case by the familiar[59] function of the general interactions $f(\varepsilon, n)$. This relation for characteristic SP is illustrated in Fig. 2 (according to the data of Kholmanskii and co-workers[15,66,67]). The orbital nature of the electronic transition and the change in

the dipole moment of the molecule in this transition can be determined from the qualitative and quantitative analysis of these relations. In particular, in the case of SP_{34} the presence of a break in the relation between ν_M and $f(\varepsilon, n)$ for $f \cong 2$ demonstrates the involvement of the electrons of the isolated n orbital of the oxygen in the oxaindan ring in the transition (2). The specific interactions of the highly polar and OH-containing solvent molecules with the n orbital of SP_{34} lower the ground level of this compound. As a result of the summation of the effects of the universal and specific interactions, ν_M hardly changes when $f > 2$, while under conditions where $f < 2$ the dependence of ν_M on $f(\varepsilon, n)$ for SP_{34} has almost the same slope as for SP_3, SP_4, SP_{26}, and MA (Fig.2 [69]). This indicates the similarity of the changes in the dipole moment of the SP on excitation of the transition in the A ring and in the transition (2).

However, the dipole moment changes appreciably when the oxygen heteroatom in the A ring is replaced by nitrogen (as in SP_{11}) and sulphur (as in SP_{24}) (Fig.2). Evidently, as a consequence of the changes in I for the D ring and ε_A for the A ring of SP_{11} and SP_{24}, the transition (2) in these SP has a significantly greater energy than the transition in the A ring.[68,70] On the basis of the dependence of ν_M on $f(\varepsilon, n)$, it is possible to estimate the charges on the heteroatoms in the DSA* states of the (π, π^*) type[21,66] which will be designated for brevity as states of the N type (Table 4).

Table 4. The orbital nature, the charges on the heteroatom (q), the lifetimes (τ_t), and the constants for the quenching by triphenylamine of the triplet states of spiropyrans (k_q^{TPA}) in toluene.[23,27,55,66]

SP	State	τ_t, s	k_q^{TPA}, litre mol^{-1}s^{-1}	q, e
SP_1	L	10^{-6}	$6\cdot10^5$	~0.1
SP_2	L	—	$<6\cdot10^5$	<0.1
SP_3	N	10^{-9}	$4\cdot10^9$	0.4
SP_7	N	$6\cdot10^{-10}$	—	—
SP_{12}	N	$1.5\cdot10^{-8}$	$9\cdot10^8$	0.4
SP_{22}	L	$<10^{-8}$	—	$\leqslant0.1$
SP_{22}	($\pi,\pi^*\pi_n^*$)	10^{-6}	$3\cdot10^7$	$\ll0.1$
SP_{24}	—	—	—	0.2
SP_{26}	N	—	—	0.4
SP_{28}	L	$6\cdot10^{-5}$	$5\cdot10^5$	$\leqslant0.1$
SP_{36}	($\pi,\pi^*\pi_n^*$)	$1.5\cdot10^{-8}$	10^8	$\ll0.1$
SP_{38}	($\pi,\pi^*\pi_n^*$)	$2\cdot10^{-5}$	$6\cdot10^7$	$\ll0.1$

In SP with the naphthopyran ring containing the nitro-group, the first electronic transition is of the $\pi-\pi^*\pi_n^*$ type.[27] The involvement of the l electron in excitation is improbable[18,27] and the charge on the nitro-group is transferred mainly from the naphthalene ring.

All the SP with the nitro-group phosphoresce at 77 K.[6,21,27,66] In addition, the fluorescence of SP_{19} in liquid solution at room temperature has been observed.[71] The phosphorescence spectrum of SP_3 has a vibrational structure. It follows from its analysis, carried out by Khamchukov et al.[72] and Gehrtz et al.,[73] that the stretching (symmetrical) and deformation vibrations of the nitro-group are manifested in the spectra. The frequencies of these vibrations differ appreciably for SP and MA.[68] The 0–0 transition frequency ν_{00} in the case of the phosphorescence of SP with the nitro-group in the benzopyran ring can be both greater and smaller than the ν_{00} for the phosphorescence of the corresponding nitrochromene, depending on the structure of the D ring.[68,69] For example, for SP of the type of SP_3 and SP_4, the frequency ν_{00} is greater by ~700 cm^{-1} than for the phosphorescence of the corresponding MA and the quantum yield ϕ_{ph} of the phosphorescence of the SP exceeds by a factor of three that for the MA.[69] These differences are apparently caused by the interaction of close levels of the (DSA*) and (D^+SA^-)* singlet and triplet states of the SP.

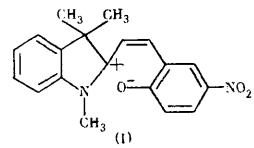
The position of the 0–0 band in the phosphorescence spectra of spiropyrans with the nitro-group is almost independent of the nature of the solvent.[6,29,48,72,73] On the other hand, in the case of SP_2 this band undergoes a hypsochromic shift by ~2000 cm^{-1} on replacement of the non-polar matrix by a polar one or by a hydroxylated matrix.[29,48] The phosphorescence lifetime of SP having the nitro-group and the corresponding nitrochromenes varies from ~0.03 to 0.3 s. The phosphorescence excitation spectrum of SP_3 coincides with the absorption spectrum within the limits of the first absorption band in solvents of the type of petroleum ether, propanol, and tetrahydrofuran (THF).[30,72] These results make it possible to assign the phosphorescence state of SP with the nitro-group in the benzopyran ring to the ^3N type and in the case of SP_2 to the ^3L type.

The high values of the intersystem inversion constant K_{ST} for SP with the nitro-group are due to the presence of intermediate $^{1,3}(n, \pi^*)$ levels of the nitro-group, at least one of which is located between the $^{1,3}N$ levels.[15,66,68,74,75] The constant K_{ST} can reach in this instance ~10^{11} s^{-1}.[16–18,74] It follows from the analysis of the experimental data for nitroanisoles, epoxynitroindalone, and nitronaphthalenes[76–78] and from theoretical calculations that the energy of the $^1(n, \pi^*)$ level for SP with the nitro-group is ~27500 cm^{-1} and that of the $^3(n, \pi^*)$ level is 23500 cm^{-1}–24500 cm^{-1}.

The fluorescence of the spironaphthopyrans SP_{22}, SP_{23}, and SP_{28} arises from the $^1(\pi, \pi\pi_n^*)$ state and the simultaneous presence of both fluorescence and phosphorescence shows that the $^{1,3}(n, \pi^*)$ levels of the nitro-group lie above the energy level of the (π, $\pi^*\pi_n^*$) state.[27,79,80] The sharp differences between the fluorescence and phosphorescence intensities of SP_{22}, SP_{23}, and SP_{28} indicate different positions of the ^3L and $^3(\pi, \pi^*\pi_n^*)$ levels in these compounds and hence a different nature of the phosphorescent states.

Only fluorescence is observed for SP without the nitro-group (SP_1 and SP_{21}),[65,81,82] but one can postulate that the lowest triplet level of SP_1 has an energy close to that of the phosphorescent level of SP_2.

The following facts are known about the luminescence-spectroscopic characteristics of the SP photoproducts. The coloured form (B) exhibits only an intense fluorescence.[6,7,15,30,49] In a study[73] of the photocolouring reaction of SP_3 at $T \leqslant 4.2$ K, which stops at the state involving the formation of the *cis*-cisoid isomer X, the phosphorescence band of the X isomer has been discovered (at ~15000 cm^{-1} in trimethylpentane and n-hexane). The formation of this isomer has been confirmed by the method involving the optically detectable magnetic resonance, whose use together with theoretical calculations made it possible to investigate the structure of the X isomer and to represent it in the following form:



(I)

It has been established by studying the photocolouring reactions of SP at low temperatures and in the matrix comprising the compound itself that an absorption band whose

frequency is close to the absorption band of the thermodynamically more stable *trans*-isomer of the *B* form corresponds to the *cis*-cisoid isomer of the *B* form of SP such as SP_3 or spironaphthopyrans with and without the nitro-group.[6,35,49,50,54,80]

. Spectrokinetic Studies on Photochromic Transformations f Spiropyrans

The spectrokinetic studies on photochromic reactions of SP, carried out under both photostationary conditions and with the aid of pulse (mainly laser) techniques proved fruitful for the elucidation of the orbital nature and the energy of the PCA state of the SP and for the determination of the photocolouring reaction mechanism. We shall not dwell on a large number of studies of the kinetics of the reactions of the coloured form of SP in which the influence of the structure of the SP and the nature of the matrix on the rate constant for the dark decolorisation of the *B* form[55,83–89] and the molecular association processes of the SP in both *A* and *B* forms were investigated.[74,83,90–97] The association effects significantly complicate the pattern of the photochromic reactions of the SP, particularly in aliphatic solvents and at high SP concentrations but do not influence appreciably the primary intermolecular photophysical and photochemical processes over a wide range of SP concentrations (10^{-6}–10^{-4} M)[97] in weakly polar solvents.

We shall analyse in the first place the results of the study of the quenching of the photocolouring reactions of SP by various quenching agents under photostationary conditions. These studies were performed to elucidate the question of the involvement of the triplet state of the SP in the photocolouring reaction and to determine its orbital nature.

The following results were obtained in experiments on the quenching of the photocolouring reaction by molecules with a low energy of the *T* state (anthracene, etc.) and electron donors. The reaction involving the photocolouring of SP having the nitro-group in the indoline and naphthopyran rings in weakly polar solvents proceeds 100% via the triplet state, while in SP with the nitro-group in the benzopyran ring it proceeds via this state to an extent not less than 70%.[23,27,29,98,99] The results of the estimation of the lifetimes of the lowest triplet states of SP (including PCA) are presented in Table 4. The quenching of the SP photocolouring reaction by electron donors is due to the deactivation of the triplet state as a result of electron transfer in a triplet exciplex between the SP and the electron donor.[23,99,100–102]

The quenching rate constant k_q depends on *I* for the electron donor and ε_A for the spiropyran in the excited state. For example, for tetramethyl-*p*-phenylenediamine (TMPP), it is close to the diffusion rate constant regardless of the SP structure.[23] Conclusions concerning the orbital nature of the deactivated triplet state of various SP have been reached from a comparison of the k_q for the same electron donor having a higher *I* than TMPP. These data for the case where the quenching agent was triphenylamine are listed in Table 4, from which it follows that k_q^{TPA} is correlated with *q*. The contribution of the (l, π^*) configuration to the *T* state of the SP of the corresponding type and the electron affinity ε_A are determined by the positive charge *q* on the heteroatom. The negative charge is in this case localised on the nitro-group and ensures, for example, the effective formation of hydrogen-bonded complexes between the proton-donating additive in the SP or another aromatic nitro-compound in the excited state.[6,76,103,104]

The low values of τ_T (Table 4) are due to the rapid intramolecular deactivation of the triplet state as a result of the reaction yielding the coloured form. This evidently also

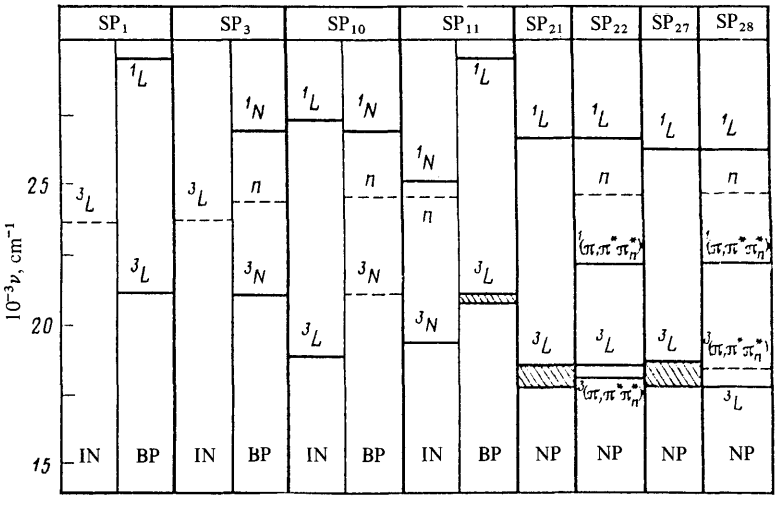


Figure 3. Energy level diagrams for certain SP; IN, BP, and NP are the indoline, benzopyran, and naphthopyran rings of the SP.[66]

accounts for the absence of an influence of added oxygen and cyclo-octatetraene[15,71] on ϕ at concentrations of additives of ~10^{-3} and 10^{-2} M respectively. Such concentrations are insufficient for the observation of an appreciable influence by the quenching agent on the photocolouring reaction of the SP with the nitro-group in the benzopyran ring.[23,102]

Thus experimental studies have shown that both the singlet (for SP without the nitro-group) and triplet (for SP with the nitro-group) PCA states should include a definite contribution by the (l, π^*) configuration. This contribution determines the positive charge on the heteroatom in the D and A rings and, as will be shown below, the mechanism and the effectiveness of the dissociation of the C_{spiro}–O bond depend in their turn on the latter. The probability of the population of the levels of the PCA states depends significantly on the relative positions of the electronic levels of the SP. Data[15,22,27,29,68,105–107] concerning the disposition of the electronic levels of the various fragments of the SP molecule make it possible to construct a diagram of the lowest electronic levels for SP with certain characteristic structures and substituents (Fig. 3 [66]). The suggested disposition on the diagram of the levels which had not been observed experimentally is shown by dashed lines. Levels of the $^{1,3}(n\pi^*)$ type have been conventionally represented by a single level designated by n, and this also applies to the levels of the (DS*A) and $(D^+SA^-)^*$ states of SP_3, which are represented by a single N level.

III. THE MECHANISM OF THE PHOTOCOLOURING REACTION

The principal question concerning the mechanism of the photodissociation of the C_{spiro}–O bond and the formation of the B form is how the redistribution of electron density arising on excitation of the π-electron system of the SP ensures the weakening of the C_{spiro}–O σ-bond and what role the vibrational excitation of the SP molecule plays in the bond dissociation.

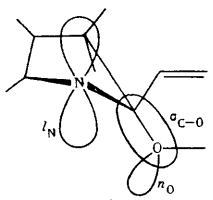
The intramolecular photophysical and photochemical processes are unambiguously determined by the orbital nature of the electronically excited state of the SP, which specifies the initial redistribution of electron density, regulating both the mechanism of the interaction of the electrons of the C_{spiro}–O σ-bond with other electrons of the molecule and the mechanism of the excitation of particular vibrations in the molecule. The orbital nature of the electronically excited state of the SP is determined in its turn by its molecular structure. For this reason, the elucidation of the mechanism of the bond photodissociation makes it possible to relate directly the effectiveness of the photocolouring of the SP to the structure, i.e. permits the specific synthesis of SP with particular photochromic properties.

1. The Mechanism of the α-Dissociation of the C_{spiro}–O Bond

The quantum yields of the photocolouring reaction of SP with the nitro-group in the indoline ring are fairly high and comparable to the ϕ for SP with the nitro-group in the benzopyran ring (Table 1). On the other hand, the energy of the electronic excitation of these SP on irradiation with light at the wavelength corresponding to the first absorption band is fully localised in the indoline fragment regardless of the type of substituent in the benzopyran ring (Fig. 3 [21,25]).

For SP with an analogous disposition of the levels but with a different orbital nature of the lowest triplet state, the values of ϕ are significantly smaller than for SP of the SP_3 type (cf. with SP_{10} in Fig. 3 and in Table 1). The principal difference between the orbital nature of the lowest triplet state of these SP consists in a much greater positive charge on the nitrogen heteroatom in the ^3N state of SP of the SP_{11} type than in the ^3L state of SP of the SP_{10} type.

On the basis of data for the structure of SP (see Section II), their central part can be represented as follows:



(II)

Here the axis of the l orbital of oxygen is perpendicular to the plane of the figure. It follows from XD data for SP that the solid angle between the l_N orbital and the σ_{C-O} bond is 10–30°. Bearing in mind their close proximity, one can postulate the interaction of the electrons of these orbitals. In the gound state of the SP, such interaction is referred to as the anomeric effect.[21,108] Its essential feature consists in the mixing of the l_N orbital and the unoccupied antibonding σ^*_{C-O} orbital. As a result of this interaction, the C_{spiro}–O bond is weakened even in the ground state.[36–41]

We shall now discuss the orbital nature of the N-type triplet PCA state of SP_{11}. It follows from Section II, that the luminescence-spectroscopic characteristics of SP with the nitro-group in the indoline ring virtually coincide with the corresponding characteristics of p-nitroanilines and are close to the characteristics of p-cyano-N,N′-dimethylaniniline.[109] For the latter compound it is known[110] that the dipole moments of the molecule in the ^1N state ("b") and in the biradical state with "twisted" configuration ("a") are virtually identical. This makes it possible to represent the structure of the precursor of the state "a", namely the Franck–Condon state "b", also in the form of a biradical in which the unpaired electrons are localised on the nitrogen atom of the CN group.

Taking into account these data and using the one-electron approximation, the N-type Franck–Condon state of SP_{11}, in which there is an appreciable positive charge on the nitrogen atom, can also be represented by a biradical. Consequently the l_N orbital in the $^{1,3}N$ states of SP_{11} has a radical character and this leads to the exchange interaction of the electrons of the l_N and σ_{C-O} orbitals, which constitutes the basis of the mechanism of the α-dissociation of the bonds (type 1 Norrish reaction[19,20,100]). The vibrationally excited radical-cations of amines and various carbonyl compounds dissociate according to this mechanism.[19,100,111–113] In SP of the SP_{11} type, the vibrational excitation of the spiro unit (II) is also essential for the dissociation of the C_{spiro}–O bond via the α-mechanism.[113] Under these conditions, the most effective are the low-energy deformation vibrations of one heterocycle relative to the other, in which the solid angle between the axes of the l_N and σ_{C-O} orbitals diminishes. The torsional vibrations of the heterocycle are less effective in this respect, although their excitation can increase sharply the probability of the non-radiative relaxation of the electronically excited state of the SP [114] with formation of the B form.

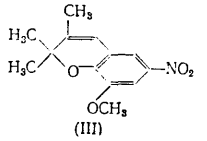
Together with the dissociation of the C–O bond, the dissociation of the C_{spiro}–C(3′) bond in SP with the nitro-group in the indoline ring can also dissociate via an analogous mechanism. Presumably this reaction ensures the irreversible decomposition of the given SP which has a lower photostability than SP with a nitro-group in the benzopyran ring.[115]

The effectiveness of the dissociation of the C_{spiro}–O bond via the α-mechanism is fully determined by the electronic structure of the indoline ring in the ^3N state. The introduction of various substituents into the benzopyran fragment of an SP containing the nitro-group in the indoline ring has virtually no effect on the yield ϕ.[21,25,102]

Since, like the nitro-group, the acetate group is an electron-accepting substituent, its introduction into the 5-position renders the lowest triplet state a highly polar CT state. It follows from the data of Gal'berstshtam and co-workers[9,89] that the disposition of the electronic levels of SP_{15} is analogous to that in SP_{11}. Taking into account these data, it is possible to postulate also for SP_{15} a mechanism for the α-dissociation of the C_{spiro}–O bond, which explains the fairly high value of ϕ_{365} for this SP (0.24) compared with ϕ_{365} for SP_{10} (Table 1).

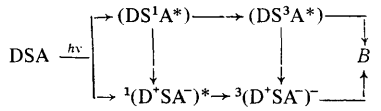
Thus the α-dissociation mechanism, well known in the photochemistry of organic compounds, makes it possible to explain the high effectiveness of the cleavage of the C_{spiro}–O bond in the formation of the *B* form of SP with an electron-accepting substituent in the indoline ring.

We shall consider the mechanism of the photodissociation of the bond in indoline SP with the nitro-group in the benzopyran ring and SP with other D and A rings (xanthene, oxaindan, etc.). Before doing this, we may note that the mechanism of the bond cleavage in the MA



(III)

proceeds to the extent of 80% via *N*-type *T* state and the quantum yield of the *B* form of compound (III) is 0.7.[116] On this basis, one can assume that the (DS^3A^*) state of SP is likewise a PCA state. Furthermore, in the case of indoline SP with the nitro-group in the benzopyran ring, the positive charge is localised in the $(D^+SA^-)^*$ states on the nitrogen atom of the D ring,[28,117,118] while the negative charge is localised on the nitro-group.[103,118,119] Consequently the electronic structure of the given states ensures bond dissociation via the α-mechanism. Thus the high values of ϕ for the spiropyrans of SP_3 type are due to the fact that both lowest ^3N states of the (DSA*) and $(D^+SA^-)^*$ types are PCA states and that the photocolouring reaction proceeds via the mechanism



(3)

The probability of bond dissociation on excitation in the PCA states of SP is determined by the charge *q* on the oxygen and nitrogen atom. The latter depends in its turn on the change in the dipole moment of the molecule, which is correlated with the dipole moment of the transition |M| for transitions with intramolecular CT.[15]

The value of |M| is related to the experimental characteristics of the CT band:[120]

$$|M| = 0.0958\,(\Delta\nu_{1/2}\varepsilon_M\nu_M^{-1})^{1/2}, \qquad (4)$$

where $\Delta\nu_{1/2}$ is the half-width of the CT band. Assuming that ϕ is proportional to *q*, it is possible to obtain with the aid of Eqn.(4) the relation between ϕ and the intensity of the first absorption band of the SP with the nitro-group. Fig. 4 presents the dependence of ϕ on $(\varepsilon_M\nu_M^{-1})^{1/2}$ for a series of SP. Its linearity demonstrates the validity of hypotheses[15,21,102] concerning the dependence of the mechanism of the photodissociation of the bond in SP on its structure.

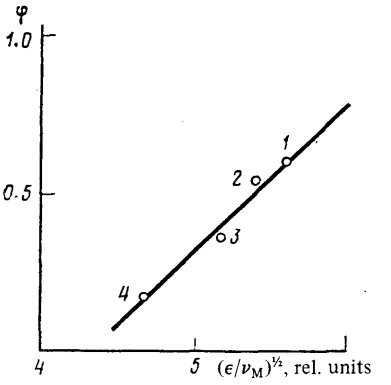
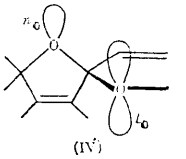


Figure 4. Dependence of ϕ on $(\varepsilon/\nu_M)^{1/2}$ for different SP: 1) SP_3; 2) SP_6; 3) SP_{33}; 4) SP_8 (the values of ε and ν_M have been taken from Kholmanskii et al.[15]).

The occurrence of the transition (2) and the corresponding states $(D^+SA^-)^*$ in SP of the SP_3 type makes it possible to explain readily the dependence of the probability of the photoionisation of the SP on its structure in the presence of an external electron acceptor.[28,117,121,122] Scheme (3) can also be used successfully to account for the intra- and intermolecular photochemical processes occurring on UV irradiation of an SP_8 single crystal at 77 K,[123,124] since the key factor in these studies was the assumption of the formation of the $^3(D^+SA^-)^*$ states via the tunnel electron transition between the D and A rings in the (DSA*) state of the SP. The orbital nature of the (DSA*) state ensures, with the corresponding probability, the α-dissociation of the C_{spiro}–N bond, which may be the basis of the irreversible photodecomposition of SP of the SP_3 type.

On the basis of XD data for the structure of SP_{34}, its spiro-unit can be represented as follows:



(IV)

On excitation of the $(D^+SA^-)^*$ states in SP_{34}, the positive charge is localised on the oxygen atom of the oxaindan ring and its n_O orbital assumes a radical character (see Section II). Since the n_O orbital is almost orthogonal in relation to the σ orbital of the C_{spiro}–O bond [see structure (IV)], the exchange interaction between the electrons of these orbitals is unlikely. As a result, the $(D^+SA^-)^*$ states of SP_{34} are not PCA states. The lower yield ϕ for SP_{34} compared with SP_3 (Table 1) and the temperature dependence of ϕ for SP_{34} [33] show that the levels of the $^{1,3}(D^+SA^-)^*$ states are below the levels of the PCA states of the (DSA*) type.

As in a study by the authors of the review,[27] the following scheme can be formulated for SP_{34}:

$$\mathrm{DSA} \xrightarrow{h\nu} \begin{cases} \rightarrow (\mathrm{DS^1A^*}) \longrightarrow (\mathrm{DS^3A^*}) \longrightarrow B \\ \qquad\qquad \downarrow\uparrow kT \qquad\qquad \downarrow \\ \rightarrow {}^1(\mathrm{D^+SA^-})^* \rightarrow {}^3(\mathrm{D^+SA^-})^* \rightarrow \mathrm{DSA} \end{cases} \qquad (5)$$

The energy difference ΔE between the (DS^3A^*) and $^3(D^+SA^-)^*$ states of SP_{34} is close to the activation energy E_a for the photocolouring reaction[27] and can be estimated by comparing the known values of E_a for other SP. E_a for SP_{34} is greater than for SP_3 (~0.04 eV) [29] but smaller than for SP_{22} and SP_{36} (~0.15 eV),[27] since $\phi = 0$ for SP_{34} at 77 K and does not change appreciably in the range 180–250 K.[33] Consequently an estimate in the range $0.04 < \Delta E < 0.15$ eV is valid for $\Delta E \cong E_a$. For such a low value of ΔE, the PCA state of the (DS^3A^*) type is effectively populated via a thermal mechanism.

The structure of the xanthone ring also fails to ensure conditions essential for bond dissociation via the α-mechanism in the $(D^+SA^-)^*$ states.[21,102] The more significant decrease of ϕ for SP_{26} compared with SP_3 (Table 1) is apparently caused by the increase of ΔE to such an extent that the thermal population of the PCA state of the (DS^3A^*) type becomes improbable and the state is almost completely deactivated owing to the transition $(DS^3A^*) \rightarrow {}^3(D^+DA^-)^* \rightarrow$ DSA.

In SP of the SP_{24} type, the valence orbitals of the sulphur atom are sp^3-hybridised,[40] which diminishes the degree of their conjugation with the π-electron system of the benzene ring and the charge q in the ^1N state (Table 4). The values of I for the indoline and benzopyran rings are similar.[70] On the basis of these data, one can postulate that the levels of the $(D^+SA^-)^*$ states lie above the corresponding levels of the (DS*A) states and that the α-dissociation of the C_{spiro}–S bond is unlikely; the photocolouring reaction of the given SP therefore proceeds with a fairly high value of ϕ via the (DS^1A^*) state[34,40] in accordance with the predissociation mechanism (see below). Thus, using the known[15,21,24,26,70,125,126] features of the changes in the intensity and energy of CT transitions (within the ring having the nitro-group and between the orthogonal rings) as a function of the structure of the SP and the nature of the matrix and also by invoking the α-dissociation mechanism, it is possible to explain successfully and to predict the photochemical activity of SP.

2. The Role of Vibrational Excitation and the Mechanism of Bond Predissociation in SP

Studies of the influence of the vibrational excitation of the electronically excited state on the kinetics of the photochemical reaction are of undoubted interest. For SP with the nitro-group, the photocolouring reactions proceed mainly via the formation of the triplet state: the vibrational excitation of the PCA state is essential to ensure the effective interaction of the orbitals of the orthogonal rings, which constitutes the basis of the α-dissociation mechanism. The energy of the electronic excitation, equal to the difference between the energies of the S_1 and T_1 states (5000–6000 cm^{-1}), may be expended on this vibrational excitation.[16,66] This excitation is also necessary to ensure that the atoms whose bond is ruptured can move apart to a sufficient distance to avoid recombination.[19]

SP with the naphthopyran heterocycle (SPN) are characterised, like their benzopyran analogues, by high yields ϕ (Table 1). However, the increase in the length of the π-electron system changes the disposition and orbital nature of the lowest electronically excited states of SPN (Table 3), as a result of which their photophysical and photochemical properties are also altered. In particular, the yields ϕ for SPN without the nitro-group depend only very slightly on th nature of the solvent and of the second heterocycle (Tables 1 and 3). This is a consequence of the photocolouring reaction of the given SP via a singlet state in accordance with a mechanism different from the α-dissociation mechanism.[22,24,27] It has been established[22] that the dissociation of the C_{spiro}–O bond in the ^1L state requires the excitation of the SPN at least to the first vibrational level of the given state. The vibrations whose nature is that of the vibrations of the COC group (see Section II) and their excitation promote the non-radiative transition $A^* \rightarrow X$ under these conditions. The same transition is evidently responsible for the decrease by a factor of two of the intensity of the fluoresence of SP_{21} on increase of the frequency of the exciting light from ν_{00} to $\nu = \nu_{00} + 500$ cm^{-1}.[65] In conformity with these features, the yield ϕ tends to zero on excitation of the SPN by light having a frequency ν close to ν_{00}.[22]

In the irradiation with light having $\lambda = 365$ nm ($\nu_{365} = 27\,400$ cm^{-1}) of the spiropyrans SP_{29}, SP_{35}, and SP_{37}, the energy of the light quantum is lower than the energy of the 0–0 transition ($h\nu_{00}$), whose frequency can be determined from the absorption spectra. For SP_{35}, SP_{29}, and SP_{37}, this frequency is 28750, 28640, and 28500 cm^{-1} respectively.[22,23] In this case the photocolouring reaction takes place because light with $\lambda = 365$ nm is absorbed by vibrationally and rotationally excited SPN molecules in the ground electronic state. Consequently ϕ_{365} for these SP should be proportional to the number $n^\#$ of such molecules, which is determined by the Boltzmann distribution $n^\# = n\exp[-\Delta\nu/kT)]$, where $\Delta\nu = \nu_{00} - \nu_{365}$.

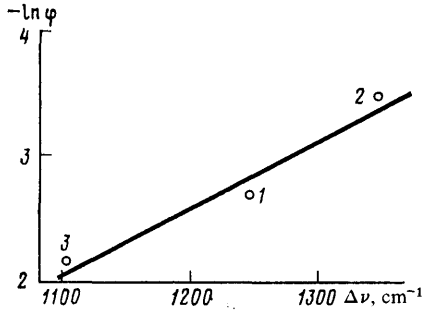


Figure 5. Dependence of $-\ln\phi$ on $\Delta\nu$ for SP: 1) SP_{29}; 2) SP_{35}; 3) SP_{37} (the values of ϕ and ν have been taken from Kholmanskii[22] and Kholmanskii and Lokshin[33]).

Thus $\ln\phi$ should be directly proportional to $\Delta\nu$. Fig. 5 presents the dependence of $-\ln\phi$ on $\Delta\nu$ for a series of SPN, from the slope of which it is possible to determine T. It proved to be 250 ± 10 K, i.e. was virtually identical with the temperature at which ϕ_{365} had been determined for these SP.[22,33] The result constitutes additional confirmation that the photocolouring reaction of the SPN without the nitro-group proceeds via the ^1L state of the vibrationally excited SPN molecule. Under these conditions, light with $\lambda = 313$ nm excites either the higher vibrational levels of the S_1 state or the S_2 state is excited. The maximum value $\phi \cong 0.6$ (Table 1) is obtained in both cases. It follows from the temperature

variation of ϕ for SPN with the nitro-group that E_a for the photocolouring reaction exceeds ΔE, which is equal to the difference between the energies of the ^3L-type PCA state and the lowest $^3(\pi, \pi^*\pi_n^*)$ state by ~600 cm^{-1} and is close to the frequency of the first vibrational quantum.[27]

These results suggested[22,35] that the bond dissociation in SPN proceeds via the predissociation mechanism. The role of the dissociative level is then assumed by the electronic level of the *cis*-cisoid isomer *X*, which intersects the level of the PCA state in the vicinity of its first vibrational level. The formation of the isomer *X* leads to the isomerisation mechanism for the degradation of the electronic excitation energy to vibrational energy.[6,127,128] On the basis of the results described and using the data[6,7,35] for the E_a for the forward and reverse thermal formation reactions of the coloured form of SP, it is possible to represent the path followed in the photochemical and thermal formation reactions of the isomer *X* in the *B* form by potential energy curves and the transitions between them can be illustrated (Fig.6).

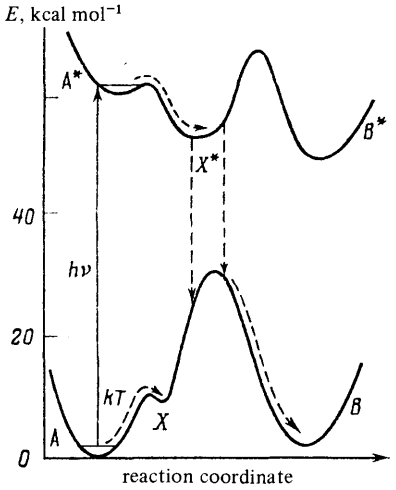
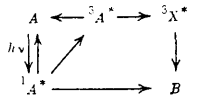


Figure 6. The potential energy surfaces for the ground and electronically excited states and the thermo- and photocolouring reaction pathways of SP [35].

3. The Nature of the Short-Lived Products arising in the Flash Photolysis or Pulse Radiolysis of Spiropyrans. The Mechanism of the Photocolouring Reaction

Numerous studies have been made of reaction (1) by the method of kinetic pulse spectroscopy (especially laser spectroscopy).[55,74,90,99,116,128–141] The time resolution of pulse apparatus has been increased at the present time to the picosecond range.[74,97,132,140] The values of λ_{max} obtained in the above studies, characterising the absorption by short-lived products, and their lifetimes are listed in Table 5. An especially large number of studies have been devoted to SP containing a nitro-group. It has been established for SP_1 and SP_{21}[15,55,81,91,128] that the photocolouring reaction proceeds via the ^1A state. Only the absorption bands of the coloured form but not of the short-lived products are observed in the spectra of the photoproducts at least in the time range $\geq 10^{-7}$ s. The *T*–*T* absorption spectrum of SP_1 has been obtained by means of the sensitised population of the T_1 level via the *T*–*T* energy transfer mechanism.[128]

The photocolouring reaction of the nitrochromene(III) and the 3,3-dimethylpiperidine SP with the benzopyran ring has been investigated by laser flash photolysis.[116,141] The following process scheme, analogous to scheme (1), has been proposed for compound (III):



(6)

The absorption spectra of the states ^3A, ^3X, and *B* are similar and can be distinguished only kinetically using the differences between their lifetimes, which are 80 ns, 400 ns, and 0.1 s respectively. The quantum yields in the formation of *B* via ^1A and ^3A are in the ratio 1 : 4, their sum amounting to 0.7, while the quantum yield of the state ^3A is 0.7.

Table 5. Spectrokinetic characteristics of the short-lived products of the photolysis and radiolysis of spiropyrans.

SP	Method of study	Δt, s	Matrix	λ_{max}, nm	τ, s	Refs.
SP_1	l.p.	10^{-8}	ch	480	$6\cdot10^{-7}$	[128]
SP_3	f.p.	10^{-5}	t	440	$5\cdot10^{-4}$	[129]
	f.p.	10^{-6}	mch	430	10^{-3}	[130]
	l.p.	10^{-8}	mch	430	$1.5\cdot10^{-7}$	[96]
	l.p.	10^{-8}	ms	430, 600	$2.5\cdot10^{-7}$	[96]
	l.p.	10^{-9}	t	430	10^{-8}	[131]
	l.p.	10^{-9}	e	430, 570	10^{-8}; 10^{-7}	[131]
	l.p.	10^{-9}	pmma	460	—	[131]
	l.p.	10^{-11}	t, e	430, 580	10^{-9}—10^{-8}	[132]
SP_4	f.p.	10^{-4}	t	445	$5\cdot10^{-4}$	[129]
	f.p.	10^{-6}	t	440	10^{-3}	[99]
	f.p.	10^{-6}	ee	480—520	0.2	[133]
	l.p.	10^{-9}	t	420	10^{-8}; 10^{-6}	[131]
	l.p.	10^{-9}	e	440, 470	—	[131]
	l.p.	10^{-9}	pmma	470	—	[131]
SP_5	f.p.	10^{-6}	pmma	470, 530	0.2	[133, 134]
SP_6	l.p.	10^{-8}	b	440	$2\cdot10^{-7}$	[137]
	l.p.	10^{-8}	e	445	$3\cdot10^{-7}$	[137]
	l.p.	10^{-8}	an	460	$9\cdot10^{-7}$	[137]
	l.p.	10^{-9}	t, e	450	10^{-7}	[131]
SP_7	l.p.	10^{-8}	b	450	$5\cdot10^{-6}$	[135]
	l.p.	10^{-8}	ppg	450	$3\cdot10^{-5}$	[135]
	l.p.	10^{-8}	ms	450	$2\cdot10^{-6}$	[135]
SP_{16}	p.r.	10^{-8}	b	430	$2\cdot10^{-6}$	[139]
SP_{17}	l.p.	10^{-9}	t	440	10^{-6}	[97]
	l.p.	10^{-9}	an	440	10^{-8}; 10^{-6}	[97]
SP_{20}	l.p.	10^{-11}	b	440	10^{-8}	[140]
SP_{23}	l.p.	10^{-8}	b	470, 530	10^{-6}	[138]
Nitrochromene (III)	l.p.	10^{-8}	t	330, 520	$8\cdot10^{-8}$; $4\cdot10^{-7}$	[116]

Notation: f.p. = flash photolysis, l.p. = laser photolysis, p.r. = pulse radiolysis, Δt = time resolution of the method, ch = cyclohexane, mch = methylcyclohexane, t = toluene, e = ethanol, ee = 2 : 1 ethano–ether mixture, b = benzene, an = acetonitrile, ppg = poly(propylene glycol), ms = micellar solutions, pmma = poly(methyl methacrylate).

Scheme (6) is also valid for the piperidine SP with the sole difference, that, owing to steric factors, the reaction stops at the stage involving the formation of the isomer *X* and not *B*.

The formation reaction of the coloured form of SP with the nitro-group by pulse radiolysis in benzene proceeds via mechanisms similar to that described by scheme (6) or more precisely via the "triplet channel":[55,139]

$$A \xrightarrow{^1C_6H_6} {}^3A \rightarrow {}^3X \rightarrow A \quad (7)$$
$$\qquad\qquad \downarrow O_2$$
$$\qquad\qquad B$$

The lifetime of the state ^3A is $\leqslant 10^{-8}$ s, while that of ^3X is 2×10^{-6} s (in the absence of oxygen). The presence of atmospheric oxygen accelerates the reaction $^3X \rightarrow B$, increasing thereby the yield of *B*.

The influence of various quenching agents (oxygen, TMPP, and triphenylamine) on the kinetics of the decrease of the intensity of the short-lived absorption band of the SP_4 solution in toluene at 440 nm has been investigated[99] by flash photolysis using the results of a study of the quenching of the photocolouring reaction in photostationary experiments. This absorption disappeared with the rate constant $\geqslant 10^5$ s^{-1} and did not arise in the presence of O_2. The results obtained show that the photolysis of SP_4 proceeds via a mechanism analogous to mechanisms (6) and (7) and that the absorption band at 440 nm constitutes a superposition of the absorption bands of two SP photoproducts— ^3A and ^3X.[99] Oxygen and the electron donor deactivate ^3X and ^3A respectively under these conditions.

Thus, on the basis of the results of a number of studies,[4,99,116,139,141] and taking into account the fact that in the photostationary colouring of SP with the nitro-group the reaction proceeds mainly via the triplet state, one can postulate that scheme (6) is valid for SP with the nitro-group, as for compound (III), with the sole difference that the deactivation of the ^3X state by oxygen in the case of SP leads to the formation of the *B* form, while in the case of compound (III) the initial form of the nitrochromene is regenerated.[116]

We shall analyse from this standpoint other studies of the photocolouring reaction by the laser flash photolysis method. The short-lived spectra of SP_3 and SP_{20} arise over a period of only $\sim 10^{-11}$ s [132,140] and the disappearance of the band at 580 and 440 nm in the initial instants proceeds in accordance with the same law with a characteristic time in the range 10^{-9}–10^{-8} s, depending on the solvent (toluene and ethanol). Hence it follows that these two bands belong to the same product. By analogy with other studies[130,137,142] and in view of the high rate of its appearance, Krysanov and Alfimov[132] assigned the 440 nm band to the $S_0 \rightarrow S_1^*$ absorption of the isomer *X*, assuming that it is formed from the ^1A state. Although this reaction can in fact make a definite contribution ($\lesssim$20%) to the formation of the isomer *X* and the *B* form,[97,116,141] nevertheless it is preferable to attribute the band to the overall absorption by the SP and the isomer *X* in the *T* states (^3A and ^3X respectively). This assignment makes it possible to explain the biexponential kinetics of the decrease of the absorption by the short-lived products, noted in a number of investigations[132,137,140,142] and characterised by two times τ_1 and τ_2, and also the influence of the presence of oxygen on the latter. The rapid and slow components of the kinetics of the decrease of absorption can be reasonably assigned to absorption by the ^3A and ^3X states respectively. The time τ_1 for the ^3A state is then 10^{-9}–10^{-8} s, while τ_2 for the ^3X state is $\sim 10^{-7}$ s. The time τ_1 for the ^3A state agrees well with its existing estimates (see Table 4 and Refs. 139, 143, 144). For such values of τ_1 and τ_2 and at a low O_2 concentration ($\sim 10^{-3}$ M), the quenching process, whose rate is determined by diffusion, can exert an appreciable influence only on the slow component of the decrease of the absorption by the short-lived products, i.e. on τ_2 for the ^3X state. Indeed it has been noted that τ_1 remains unchanged and τ_2 diminishes with the simultaneous increase of the yield of the *B* form in the presence of O_2.[137,139,142] The high rate of formation of ^3A is also not surprising, since K_{ST} for aromatic nitro-compounds is of the order of $\geqslant 10^{11}$ s^{-1}. For example, the maximum intensity of the *T*–*T* absorption for nitroanisoles is attained after only $\sim 10^{-11}$ s.[76] This is also promoted by the high quantum yield (0.6–0.7) for the formation of the triplet states of aromatic nitro-compounds.[76,78,145]

Analysis of the absorption spectra of the short-lived products[131,132,140] permits the conclusion that in the case of SP, as for compounds (III), the extinction coefficients of the ^3A and ^3X states and the positions of the absorption bands are similar. In the range 570–610 nm the pattern of the variation of the short-lived spectrum may become complicated as a consequence of the superposition of the absorption band of the *B* form.

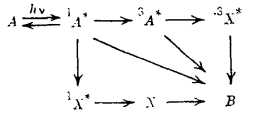
For SP_4 and SP_5, the assignment of the 440 nm band to the *T*–*T* absorption in PMMA [131] agrees with the results of a study[133] in which the identity of the lifetimes of the phosphorescence and of the short-lived absorption of SP_5 at 77 K was established. The character of the time variation of the spectrum of the short-lived product derived from SP_4 [131] permits the conclusion that the 420 nm band represents the superposition of the absorption bands of two products with appreciably different lifetimes—of the order of 10^{-8} and 10^{-6} s, which agrees qualitatively with the results of Kholmanskii et al.[99]

Biexponential kinetics of the decrease of the absorption at 440 nm have been observed for SP_{17} in acetonitrile;[97] the shorter-lived absorption was assigned by the authors to the S_0–S_1 absorption by the isomer *X*, since the decrease of the absorption intensity at 440 nm was not accpanied by an increase in the region corresponding to absorption by the *B* form (500–600 nm). However, as noted above, the constancy of the absorption intensity in the range 500–600 nm, which was observed also in other studies,[116,139,146] may be be due to the fact that the decrease of the ^3A absorption and hence also of the ^3X absorption is compensated by the increasing absorption by the *B* form.

It has been established[97] that the absorption of SP_{17} at $\lambda = 530$ nm increases with a characteristic time of 2.7×10^{-10} s (in methylcyclohexane) regardless of the initial SP concentration (the latter fact shows that the association of the SP molecules does not affect the primary photoprocesses in the molecule). This increase was attributed to the reaction $^1A \rightarrow B$ which may make a slight contribution to the formation of the *B* form in the case of SP with the nitro-group, as for compound (III).

Summing up the discussion of the results obtained with the aid of kinetic pulse spectroscopy, one may conclude that the formation of two products can be detected kinetically on apparatus with a time resolution $\leqslant 10^{-8}$ s and that the lifetime of the shorter-lived product is not appreciably influenced by oxygen. With laser pulse apparatus with a time resolution $\geqslant 10^{-7}$ s, a single short-lived product is detected as a rule, its lifetime depending on the presence of O_2. The identification of these products as the SP and the isomer *X* in the ^3A and ^3X states respectively appears to be most likely.

Thus, on the basis of the above analysis and taking into account the data in Section II and in the previous parts of the present Section, one can formulate the following general mechanism of the SP photocolouring reaction:



(8)

The scheme does not show the recombination reaction of the excited states A^* and X^* to give A and also the transitions $^1X \rightarrow {}^3X$ and $^3X \rightarrow X$ and the reverse dark reaction $B \rightarrow A$ re entirely feasible.

The occurrence of the photocolouring reaction via a particular channel is determined by the structure of the SP and external conditions. For SP containing a nitro-group, the reaction takes place mainly via the triplet channel, while for SP without the nitro-group the singlet channel is involved. Bearing in mind that the bond dissociation reaction in the ^3A state of SP_3 has an activation barrier of 0.04 eV,[29] the photochemical reaction pathway for an SP of the type SP_3 can also be represented under these conditions by the transitions illustrated in Fig. 6.

The results of the study of the kinetics of the reactions of the SP photoproducts and their lifetimes make it possible to estimate the rate constants for the transitions between them. The rate constant for the intersystem transition for SP with the nitro-group in a weakly polar solvent has values in the range $>10^{11}$ s^{-1} (transitions of the type $^1A \rightarrow {}^3A$ and apparently $^1X \rightarrow {}^3X$).[74] The rate constants for the transition $^3A \rightarrow {}^3X$ or B as well as the transition $^1A \rightarrow B$ are in the range 10^8–10^{10} s^{-1} [97] depending on the structure of the SP. The transition $^3X \rightarrow B(X)$ in the absence of oxygen is characterised by a rate constant of 10^5–10^7 s^{-1}. This applies to SP whose T state is photochemically active. If the T state is photochemically inactive, its lifetime increases to 10^{-6} s (SP_{22} and SP_{23}). The transitions between the isomers B, including the transition $X \rightarrow B(A)$, take place with a rate constant of ~10^7 s^{-1} at room temperature.[137] Since the transition $X \rightarrow A(B)$ can have activation barriers (Fig. 6 and Refs. 6 and 35), the photocolouring process can be arrested at the X-isomer formation stage as the temperature is reduced, which has in fact been observed.[35,40,73,80]

IV. PROSPECTS FOR THE EMPLOYMENT OF PHOTOCHROMIC SPIROPYRANS IN SCIENCE AND ENGINEERING

Photochromic SP have found the main application in the preparation of various recording media and in the treatment of optical information and also in the manufacture of filters with a variable optical density.[5,7,9] More than 20 light sensitive compositions of photographic materials in which SP play one role or another are patented annually in this field. Apart from their use as colour-generating components (in photochromic and free-radical photographic materials with a sensitivity up to 10^{-4} J cm^{-2},[4,147–149]), SP are also introduced as spectral sensitisers in diazotype, photopolymeric, and electrophotographic photomaterials.[7] Photochromic materials based on SP have a high resolving power (up to 10^4 mm^{-1}) and a capacity for recording and counting on a real time-scale; the light sensitivity of photochromic materials to UV light is 0.05 J cm^{-2} for a unit decrease in optical density while their sensitivity to IR irradiation is 1–2 J cm^{-2}.[4,5] The number of recording and deletion cycles on the photochromic material varies from tens to thousands depending on the optical density drop and the type of material.[5]

Photochromic materials based on SP are being improved by increasing the number of cycles which can be achieved and the light sensitivity and by creating multicolour photochromic systems and materials, which make it possible to regulate the storage time of the information recorded on them. In order to solve the latter problem, the influence of the polymer on the characteristics of the photochromic transformations and the possibility of stabilising the coloured form by selecting the appropriate polymer or the type of chemical binding of the SP to the latter are investigated[32,84,86,151–153] as is altering the structure of the SP to increase the activation barrier of the thermal decolorisation reaction.[150,151]

The light sensitivity of photographic materials based on SP, in which the image is recorded on the basis of the fluoresence of the coloured form of the SP, reaches 10^{-5} J cm^{-2}.[4,7] Materials of a similar type are nowadays being vigorously investigated and improved.

We shall consider in greater detail the use of SP as regulators of various physicochemical processes controlled with the aid of light. The principal property of SP which permits their use in this field is the sharp difference between the physicochemical characteristics of the coloured and colourless forms. The coloured form of the SP with the nitro-group is a highly polar merocyanine dye and hence it possesses the entire wide variety of properties characteristic of this class of dyes.

The possibility of the photocontrol of the potential difference on the surface of a membrane with the aid of SP has been investigated.[10,154] For this purpose, one uses the ability of the coloured form of the SP on the surface of the membrane to react effectively with a proton to form a positively charged product. The surface charge on the membrane and hence the potential difference is regulated in this way.

The possibility of using SP for the investigation of the photoregulation of ion transport through a biological membrane is extremely attractive,[154–156] particulaly the photocontrol with the aid of SP of the transport of metal salts (KCl and NaCl) and aminoacids through liquid membranes. By means of an SP, using the photochromic properties of its hydrochloride, it is possible to control the electrical conductivity of liquid solutions by means of light.[157]

The possibility of the photoregulation and investigation of the chemical reactivity of biological molecules by introducing SP into their compositions appears promising. Thus interesting studies have been made on the photocontrol of the chemical reactivity of the SP-modified α-amylase.[158–161] The mechanism of the influence of SP on the chemical reactivity of compounds is based on the change in the distribution of electron density in the molecule under the influence of the charges of the highly polar B form. The same property of the coloured form determines also the possibility of using SP as surfactants, capable of altering the surface tension at the interface between two liquids[162,163] and also of regulating with the aid of light the hydrophilicity of the polymer surface.[164–166]

The use of SP as light-sensitive additives in films and Langmuir–Blodgett monolayers is of special interest.[11,13,14,167–169] SP modified by introducing a long saturated hydrocarbon chain into the indoline or benzopyran fragment (as, for example, in SP_{18}) are used for such purposes.

Thus it is possible to modulate fluorescence by light and also to investigate the mechanism of the energy and electron transfer between layers, regulating the distance between them with the aid of intervening multilayers consisting of different numbers of monolayers but without admixtures (for example, the thickness of the cadmium arachidate layer was 25 Å [169]).

The high rates of the intermolecular reversible photochemical processes in SP (see Section III) give rise to the hope that the use of SP in multilayers of various structure in combination with the appropriate laser pulse technique will help to create interrupters or modulators of light or electric signals, which are triggered over a period of ~10^{-11} s.

Since SP exhibit photochromic properties when adsorbed on solid surfaces,[5-8] it is of undoubted interest to introduce them as light-sensitive admixtures into ordered monolayers prepared by the chemisorption of certain compounds on solid surfaces, including oriented polymers.[170-172]

The introduction of SP into liquid crystal materials and the synthesis of molecules with liquid-crystal properties on the basis of SP make it possible to expand the range of applications of the latter.[48,173-175] The preparation of photochromic compositions in the form of micellar solutions or the use of SP with amphiphilic properties makes it possible to render visible a stream of liquid to which the SP has been added[176,177] and to apply the method of flash photolysis to the study of various problems of the hydrodynamics of liquids.

It has been suggested[178,179] that SP be used as analytical reagents for the ions of a series of metals, because the latter react with the *B* form to produce intensely coloured chelate complexes.

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