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The Nature of the Primary Photochemical Step in Spiropyrans

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The mechanisms of the photocolouring reactions of spiropyrans are considered and the vibrational mechanism for the dissociation of the $C_{(2)}$-O bond in spiropyrans is analysed taking into account the relative positions of the π,π^* and n, π^* levels. The nature of the photochemically active state in spiropyrans has been established by examining the electronic nature of the low-lying excited states in organic molecules with heteroatoms. A mechanism is proposed for the photocolouring of spiropyrans, which explains the dependence of the efficiency of the $C_{(2)}$-O bond dissociation reaction in spiropyrans on their structure. The bibliography includes 63 references.

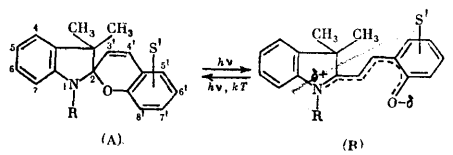
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I. INTRODUCTION

The photochromic transformations of spiropyrans (SPP) are based on a reversible intramolecular photochemical reaction. In view of the enormously wide variety of structures existing in spiropyrans[1] and the ease with which the coloured form of spiropyran can be detected, the above compounds constitute a convenient model for investigating the nature of the primary photochemical step in organic molecules with heteroatoms and its dependence on the medium and the nature of the molecule. At the same time one should note that, by virtue of their unique properties, the photochromic spiropyrans are extremely promising for practical application in various branches of science and engineering[1-4].

The overall process involving photochromic transformations of spiropyrans belonging to one of the best known subclasses—spiropyrans of the indoline series—can be represented schematically as follows[1]:



(A) (B) (1)

In the initial form of SPP the indoline and benzopyran fragments of the molecule are linked by the spirocarbon $C_{(2)}$ atom with tetrahedral sp^3-hybridisation of atomic orbitals; these

fragments are therefore orthogonal relative to one another. This was confirmed by the X-ray diffraction analysis of a single crystal of 3,3-dimethyl-8′-nitro-1-phenylspiro[indolino-2,2′-(2′*H*-1-benzopyran)].[5] Henceforth 1,3,3-trimethylspiro[indolino-2,2′-(2′*H*-1-benzopyran)] will be designated by SP_1 (see Table). The orthogonality of the indoline and benzopyran fragments of the SPP is responsible for the orthogonality of the π-electron systems of these fragments and hence justifies the assumption, to a first approximation, that the properties of the indoline and benzopyran components of the SPP are independent[1].

The coloured state of the SPP obtains following the heterolytic dissociation of the $C_{(2)}$–O bond when the hybridisation of the spirocarbon atom changes to the sp^2-type[1]. This results in the formation of planar molecules with delocalised π electrons of the indoline and benzopyran components, giving rise to an intense absorption band in the visible part of the spectrum. Merocyanine dyes can serve as a model of the coloured form of spiropyran[1]. The complex dependence of the form of the long-wavelength absorption bands of the coloured form of SPP with an electron-accepting substituent in the benzopyran component (for example, SP_2 and SP_3) on the solvent and temperature can be explained by the existence of a series of stereoisomers of form B.[1,6–12] In view of the small height of the energy barrier to the transition between the stereoisomers at room temperature, thermodynamic equilibrium is established between them in solution in less than 10^{-7} s.[6]

In a number of studies devoted to the photochromic transformations of SPP at low temperatures[8,12] and at room temperature (with the aid of laser nanosecond spectroscopy)[6,9,10], it has been established that the formation of the coloured forms of SP_2 and SP_3 proceeds via a stage involving the formation of an unstable isomer X, which is a molecule of the SPP with a ruptured $C_{(2)}$–O bond but with an unaltered molecular geometry.[12]

The coloured form of the SPP is formed when the SPP is acted upon not only by ultraviolet light at a wavelength in the region of the absorption spectrum of the initial form of the SPP but also under the influence of ionising radiation[1]. Fairly extensive data concerning the mechanism of the photocolouring of the SPP under the influence of ultraviolet light in the wavelength range 300–405 nm (this region contains the first and second absorption bands of the initial form of the SPP due to electronic transitions of the π–π* type which are localised mainly in the benzopyran component of the SPP[1]) have now accumulated, while the number of studies devoted to the photolysis of SPP under the influence of light with $\lambda < 300$ nm is so far small[1,9,13]. Analysis and interpretation of the results of the study of the photolysis of SPP by light with $\lambda < 300$ nm is complicated by the fact that, in addition to the high-energy electronic transitions localised mainly in the benzopyran component of the SPP, light at this wavelength excites also the electronic transitions in the indoline component. On the other hand, the redistribution of the electronic excitation energy of the indoline component via different channels (emission and dissipation within the indoline component, transfer to the benzopyran component) has been little investigated[1]. It has been suggested[13] that, transfer of the electronic excitation energy from the indoline to the benzopyran component of the SPP may cause the production of form B. In this sense the photocolouring of the SPP by light absorbed by its indoline component is apparently related to the photosensitised colouring of SPP.

The main question concerning the mechanism of the formation of the coloured form of SPP is how the electromagnetic radiation energy absorbed by the benzopyran component of the SPP is transformed into the $C_{(2)}$–O bond dissociation energy[1]. Tasks of practical importance, involving the discovery and explanation of the laws governing the variation of the spectral-kinetic characteristics of the photochromic transformations of spiropyrans as a function of their structure and external conditions, are closely related to the solution of this problem.

The quantum yields of the photocolouring ($\phi_{AB}^{u.v.}$) and photodecolorisation ($\phi_{BA}^{u.v.}$) of spiropyrans A with different substituents under the influence of ultraviolet light.

Spiropyran	Substituent	Solvent	*t*, K	φ_{AB}^{313} (φ_{BA}^{313})	φ_{AB}^{365} (φ_{BA}^{365})	Refs.
SP_1	1-CH_3	Hexane	173	0.1 (0.001)	—	[1]
SP_2	1-CH_3-5′,6′-benzo	Hexane	173	0.06 (0.01)	—	[1]
		Polystyrene	77	0.02	0.02	[31, 39]
SP_3	1-CH_3-6′-NO_2	Ethyl acetate	293	0.40	0.60 (0.01)	[38]
		Toluene	293	—	0.76 (0.0)	[36]
		Polystyrene	77	0.05	0.1	[31, 39]
SP_4	1-C_6H_5-6′-NO_2	Ethyl acetate	293	0.30	0.60 (0.0)	[38]
		Polystyrene	77	0.03	0.06	[31, 39]
SP_5	1-CH_3-6′-NO_2-7′-OCH_3	Ethyl acetate	293	—	0.35 (0.02)	[38]
SP_6	1-C_6H_5-6′-NO_2-7′-OCH_3	Ethyl acetate	293	—	0.35 (0.01)	[38]
SP_7	1-CH_3-6′-NO_2-7′-OC_3H_7	Ethyl acetate	293	—	0.25 (0.09)	[38]
SP_8	1-CH_3-6′-NO_2-8′-OCH_3	Ethyl acetate	293	0.30	0.45 (0.08)	[38]
		Toluene	288	—	0.59 (0.0)	[1]
		Dioxan	288	—	0.43	[1]
SP_9	1-CH_3-5′-Br-6′-NO_2-8′-OCH_3	Dioxan	288	—	0.44	[1]
SP_{10}	1-C_6H_5-6′-NO_2-8′-OCH_3	Ethyl acetate	293	0.10	0.45 (0.07)	[38]
SP_{11}	1-CH_3-6′-NO_2-8′-CH_2-CH_2	Ethyl acetate	293	—	0.55 (0.0)	[38]
SP_{12}	1-C_6H_5-6′-NO_2-8′-CH_2-CH_2	Ethyl acetate	293	—	0.55 (0.05)	[38]
SP_{13}	1-C_6H_5-6′-NO_2-8′-Cl	Ethyl acetate	293	—	0.55 (0.0)	[38]
SP_{14}	1-C_6H_5-6′-NO_2-8′-Br	Ethyl acetate	293	—	0.45 (0.01)	[38]
SP_{15}	1-CH_3-5′,7′-di-Cl-6′-NO_2	Dioxan	288	0.47	0.58 (0.015)	[1]
		Toluene	293	0.45 (0.0)	0.55 (0.0)	[1]
SP_{16}	1-CH_3-5′,6′-di-NO_2-8′-OCH_3	Dioxan	288	—	0.23 (0.04)	[1]
SP_{17}	1-CH_3-7′-NO_2	Ethyl acetate	293	—	0.17 (0.04)	[38]
SP_{18}	1-C_6H_5-8′-NO_2	Ethyl acetate	293	—	0.13 (0.00)	[38]
		Polystyrene	77	0.02	0.03	[31, 39]
SP_{19}	1-CH_3-6′-Cl-8′-NO_2	Ethyl acetate	293	—	0.05 (0.00)	[38]
SP_{20}	1-C_6H_5-6′-Cl-8′-NO_2	Ethyl acetate	293	—	0.05 (0.00)	[38]
SP_{21}	1-CH_3-4,5-benzo-6′-NO_2	Ethyl acetate	293	—	0.025 (0.015)	[38]
SP_{22}	1-CH_3-6,7-benzo-6′-NO_2	Ethyl acetate	293	—	0.015 (0.010)	[38]
SP_{23}	1-CH_3-6′-CHO	Ethyl acetate	293	0.25	0.05 (0.01)	[38]

Note. The radiation yields G_B of the coloured forms of the spiropyrans SP_2, SP_3, SP_4, SP_8, and SP_{18} in polystyrene at −77 K under the influence of γ-rays are respectively 0.07, 0.4, 0.25, 0.06, and 0.13.

The aim of the present review to analyse the existing ideas concerning the mechanism of the photocolouring of spiropyrans and their generalisation on the basis of the analysis of the nature of the electronically excited states of spiropyrans.

II. THE VIBRATIONAL MECHANISM OF THE DISSOCIATION OF THE $C_{(2)}$–O BOND

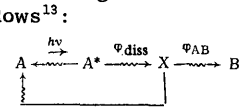
Studies have been made[13,14] on the dependence of the relative quantum yield of the fluorescence of unsubstituted chromenes and SP_2 as well as the relative fluorescence yield (ν) of SP_3 in trimethylpentane at 77 K on the wavelength of the exciting light λ_e. By analysing the vibrational absorption bands of chromenes and SP_2, the authors[13,14] established that the relative fluorescence quantum yield of the above compound decreases significantly with excitation of increasingly higher vibrational levels and that an even greater decrease of the fluorescence yield is observed when chromenes and SP_2 are irradiated with light at the wavelength

corresponding to the second absorption band. The decrease of the relative fluorescence quantum yield is explained[13,14] by the competition between the photochemical $C_{(2)}$–O bond dissociation process and the internal transition from the excited to the zero-point vibrational level, from which there is a radiative transition to the ground state.

The finding that the competition of the photochemical process is particularly pronounced on excitation of sequences of vibrations at the frequencies corresponding to the antisymmetric vibrations of the –C–O–C– group is consistent with this explanation. Three possible explanations of the vibrational mechanism of the photocolouring of SPP have been proposed[13,14]. The first applies to the case where the potential energy curve for the first excited singlet state has a "small" minimum, so that the $C_{(2)}$–O bond is ruptured after the excitation of only the first vibrational level of the S_1 state. In the second case it is assumed that the potential energy curve for an unbound excited state intersects the potential energy curve for the S_1 state near its first vibrational level. The third explanation can be used when the $C_{(2)}$–O bond is dissociated in the triplet state and the absorption of even only one vibrational quantum is sufficient for the transition of the molecule from the S_1 state to the T_0 state.

For the indoline SPP with a nitro-group in the 6′-position, a study was made of the dependence of ν on λ_e in 3-methylpentane at 77 K. The nature of this dependence is different than for the fluorescence quantum yields of chromenes and SP_2. The value of ν corresponding to SP_3 irradiated with light at $\lambda_e = 372.5$ nm was assumed to be unity; with decrease of λ_e to 323 nm, it diminishes slightly—to ~0.8; a further decrease of λ_e down to 269 nm no longer altered the above quantity. In order to account for such dependence of ν on λ_e, the authors[13] invoke the transfer of energy from the indoline component of the molecule to the benzopyran component in addition to the vibrational mechanism of the dissociation of the $C_{(2)}$–O bond. They believe that the constancy of ν starting with $\lambda = 323$ nm can be explained by the fact that at $\lambda < 323$ nm the indoline component of the molecule begins to absorb; however, since the phosphorescence of the indoline component itself is not then observed, it is suggested that the electronic excitation energy is transferred from the indoline to the benzopyran fragment, as a result of which a constant value of ν for the benzopyran component is established. In the absence of energy transfer from the indoline fragment of the molecule, ν for the benzopyran component should decrease with diminution of λ_e from 372.5 to 323 nm by an amount greater than that observed as a consequence of the competition of the photochemical $C_{(2)}$–O bond dissociation process[13].

Thus, ν for SP_3 decreases by 20% when λ_e falls from 372.5 to 269 nm, while the quantum yields of the photocolouring of this SPP under the influence of light at wavelengths of 365 and 313 nm (in 1-propanol-2-propanol mixture at 153 K) are 0.6 and 0.3 respectively[8]. It follows from these results that, firstly, the quantum yield of the photocolouring reaction (ϕ_{AB}) and the quantum yield of the photochemical $C_{(2)}$–O bond dissociation reaction (ϕ_{diss}) are different quantities. In the general case it is necessary to take into account the possibility of the reverse process—the formation of the initial form A after the dissociation of the $C_{(2)}$–O bond, i.e. the photocolouring reaction must be represented schematically as follows[13]:



(2)

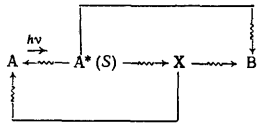
Secondly, the parallel variation of the quantum yield of the photocolouring and phosphorescence of SP_3 with λ_e shows that in this case the observed relations cannot be explained solely by vibrational mechanism of the $C_{(2)}$–O bond dissociation process and it appears that this mechanism cannot be the main mechanism of the photocolouring reaction ensuring the high values of ϕ_{AB} observed.

Indeed, the vibrational mechanism of the dissociation of the $C_{(2)}$–O bond does not take into account the nature of the electronic transition excited by light and the specific features of the electronic transition determine the efficiency of the photophysical and photochemical processes in organic molecules with heteroatoms[15,16]. Since the nature of the electronic transition actually helps to elucidate the dependence of the efficiency of intramolecular processes on the molecular structure, the vibrational mechanism of the photocolouring reaction is unsatisfactory. One should also note that, whereas in the case of chromenes the photochemical process may be the only one competing with the internal transition, on passing to the SPP with an indoline fragment, one cannot rule out the possibility also of other channels leading to a redistribution of the electronic excitation energy apart from the photochemical processes and fluorescence; in particular, one can postulate the occurrence of conformational vibrations of the molecule as a whole. The study of the vibrational mechanism of the photocolouring of the SPP should not therefore be limited to the measurement of the fluorescence or phosphorescence quantum yield; the parallel measurement of the photocolouring yield is also necessary.

III. THE RELATIVE POSITIONS OF THE LOWEST π,π^* AND n,π^* LEVELS AND THE MECHANISM OF THE PHOTOCOLOURING OF SPIROPYRANS

An attempt has been made in a number of studies[6,8–11,17–26] to explain the dependence of the photocolouring of the SPP on their structure by considering the relative positions of the lowest electronically excited states of the SPP[11,26] and also by determining the states in which the $C_{(2)}$–O bond dissociates and form B is produced[6,8–11,17–25]. The majority of these studies were mainly devoted to the elucidation of the involvement of triplet states in the photochemical colouring of the SPP. Studies have shown[18–20,22,27,28] that sensitised photocolouring due to the triplet–triplet transfer of energy from a triplet donor to the SPP is observed for all the SPP investigated, including SP_1 and SP_3. On the other hand, it was found[1,10] that the involvement of the triplet states in the direct photocolouring of the SPP is not observed for all SPP structures.

The spiropyrans SP_1 and 6′- or 7′-methoxy-SP_1 do not show an influence by oxygen on the photocolouring process[17] and exhibit neither phosphorescence[13,26] nor triplet–triplet absorption bands[8,17]. On this basis, one can assume that, on direct photoexcitation of SPP of this kind, the formation of form B takes place mainly from the excited singlet state and can be represented by the following scheme[10,11]:



(3)

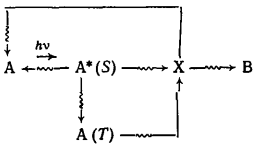
The involvement of the triplet states in the direct photocolouring of SP_3 is indicated by the presence of short-lived absorption bands due to the T_0–T_1 transition, the kinetics of the changes in which are correlated with the kinetics of the increase in the intensity of the absorption by the coloured form of the SPP[8,9,23,24]. Attempts have been made in a number of studies[21,25,28] to demonstrate the presence of the photochemically active (PCA) triplet state of the SPP with the nitro-group in the benzopyran part of the molecule by

investigating the kinetics of the photocolouring of the SPP in the presence of a triplet energy acceptor.

It has been established[21,25] that, in the presence of anthracene[25], 9-fluorenone, or benzil[21], the efficiency of the colouring of the SPP in solutions by light with $\lambda = 365$ nm is reduced. The authors of the above investigations believe that this is caused by the deactivation of the triplet PCA states of the SPP as a result of energy transfer from the SPP to the triplet energy acceptor. Calculations have shown that 83% of the coloured molecules are formed via the triplet states in the case of SP_8[25] and 20% in the case of SP_{15}[21].

However, it has been found[28] that the efficiency of the colouring of 8′-bromo-6′-nitro-SP_1 by light with $\lambda = 405$ nm is independent of the presence in solution of added anthracene (at a concentration up to 10^{-2} M). Furthermore, dissolved oxygen, which is an effective quenching agent for triplet states, does not exert an appreciable influence on the final yield of the coloured SPP molecules[1,8,21,28]. These results throw doubt on the possibility of explaining the observed decrease in the efficiency of the photocolouring of nitro-substituted SPP in terms of the quenching of their triplet states by triplet energy acceptors such as anthracene, 9-fluorenone, and benzil. If account is taken of the fact that the given compounds can show electron-accepting properties and hence there is a possibility of the phototransfer of an electron from the SPP[29-33], then one cannot rule out the probability of a chemical interaction between them and the SPP, which can lead to a decreased efficiency of the formation of coloured SPP molecules. When the SPP–anthracene system is irradiated with light at a wavelength of 365 nm, it is apparently necessary to take into account also the absorption of the initiating light by the molecules of anthracene itself.

Studies of the photocolouring and phosphorescence of SP_3 in polymeric matrices [polystyrene and poly(methyl methacrylate)] between room temperature and 75 K led to the conclusion that under these conditions the photocolouring process takes place to the extent of 100% via triplet states[20]. Thus, scheme (2) can be represented in the following general form for an SPP with a nitro-group:



(4)

As regards the electronic nature of the triplet state under consideration, the results of a number of studies[20,25,26,34,35] have shown that the triplet PCA state and the phosphorescent state of these SPP are the same triplet state of the π,π^* type. The measured energies of the triplet PCA and phosphorescence states can differ as a consequence of the influence of the medium and temperature[25]; furthermore, the dissociation of the $C_{(2)}$–O bond in the triplet state can occur at vibrational levels above the zero-point level, while emission takes place only from the zero-point vibrational level of the lowest triplet state. This may explain the fact that the triplet PCA level of SP_3 in poly(methyl methacrylate) lies above the phosphorescence level[20].

Thus analysis of the literature data shows that the photocolouring of the SPP with electron-accepting substituents in the benzopyran part can take place via the triplet state. Since the population of the lowest triplet state depends on the intercombination transition, the probability of which in heteroatomic molecules is very sensitive to the relative positions of the π,π^* and n,π^* levels[15,16,36], an attempt was made[26] to elucidate the qualitative dependence of the photochromic properties of the indoline SPP on the relative positions of the singlet and triplet π,π^* and n,π^* levels. A study was made[26] of the absorption and emission spectra of two groups of SPP. The first group consisted of SPP which are non-photochromic at room temperature (of the type of 6′-bromo-SP_1 and SP_2) and SPP with a nitro-group in the 7′-position of the naphthopyran component. The second group incorporated SPP with a pronounced photochromism at room temperature—SP_3 and SP_{23}. The authors determined the relative positions of the singlet and triplet levels of the π,π^* and n,π^* types. It was found that even if levels of the n,π^* type are present in the SPP of the first group, they lie above the $^1(\pi,\pi^*)$ level. For the SPP of the second group, at least one of the $^1(n,\pi^*)$ or $^3(n,\pi^*)$ levels lies between the $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ levels.[26] This should increase the probability of an intercombination transition for the SPP of the second group by 2–3 orders of magnitude compared with the first group[26].

On the basis of the results, it has been suggested[26] that the photochromism of the SPP at room temperature is closely related to the intercombination transition and that the colouring of the SPP with a distribution of π,π^* and n,π^* levels of the kind found, for example, in SP_3 takes place mainly via the triplet state. The observed dependence of the photochromic properties of the SPP on the relative positions of the π,π^* and n,π^* levels can be used, according to the authors[26], to explain the dependence of the photochromic properties of the SPP on their structure. This approach was also used in a study[11] of the photochromism of the SPP of the phenanthridine and diazapyrene series.

Despite the fact that the authors[11,26] were able to explain satisfactorily the dependence of the photochromic properties of the SPP on their structure, we believe that their findings are not general and do not reflect the fundamental processes responsible for the photochromism of the SPP. Indeed, the dissociation of the $C_{(2)}$–O bond is primarily an electronic process, which hardly depends on the temperature of the surrounding medium. However, the stability of the coloured form of the SPP is independent of this temperature. In the case of 6′-bromo-SP_1 and SP_2 a decrease of temperature results in their being photocoloured with an efficiency comparable to that of the photocolouring of SP_3 and SP_{23}.[1]

Apart from this, the mechanism proposed[26] for the photocolouring of the SPP does not take into account, like the vibrational mechanism of the dissociation of the $C_{(2)}$–O bond, the specific features of the electronic states in which the $C_{(2)}$–O bond is dissociated. This mechanism does not therefore permit an explanation of the change in ϕ_{AB} for the SPP as the nitro-group moved from the 6′-position to the 7′- or 8′-position or following the introduction into the benzopyran component of yet another substituent, in addition to the nitro-group; as noted above, within this series of the SPP there is a fairly considerable change in the contribution of the colouring process involving the triplet state. Furthermore, ϕ_{AB} exhibits an appreciable sensitivity also to λ_e.[1]

It is also noteworthy that the positions of the n,π^* levels are usually determined very approximately[36] in view of the low intensity of the band due to the n,π^* transitions and the superposition on the latter of the significantly more intense band of the π–π^* transitions. For example, the following sequence of low-lying excited levels has been determined for SP_3 in toluene: $S_0 < {}^3(\pi,\pi^*) < {}^3(n,\pi^*) < {}^1(\pi,\pi^*) < {}^1(n,\pi^*)$ while in another study[25] the following sequence was obtained for SP_8: $S_0 < {}^3(\pi,\pi^*) < {}^3(n,\pi^*) < {}^1(n,\pi^*) < {}^1(\pi,\pi^*)$. Therefore the rate of the intercombination transition for SP_8 should apparently be not lower than the rate of the intercombination transition for SP_3 and, according to the postulates developed

by Belaits and Platonova[26], the value of ϕ_{AB} for SP_8 should be not less than for SP_3. However, in reality the values of ϕ_{AB} for these SPP in toluene at room temperature under the influence of light with $\lambda = 365$ nm are 0.59 for SP_8 and 0.76 for SP_3.[1]

Thus the mechanism of the photocolouring of the SPP proposed on the basis of the consideration of only the intercombination transition and the SPP does not reflect, like the vibrational mechanism of the dissociation of the $C_{(2)}-O$ bond, the entire specific features of the primary photochemical step in the photochromic transformations of the SPP.

IV. THE PHOTOCHEMICALLY ACTIVE STATE OF SPIROPYRAN AND THE MECHANISM OF THE DISSOCIATION OF THE $C_{(2)}-O$ BOND

The photochemically active state of spiropyran is an excited state in which the $C_{(2)}-O$ bond is dissociated. Heiligman-Rim et al.[12] explained for the first time the dissociation of the $C_{(2)}-O$ bond by a redistribution of the electron density as a result of the excitation of the electronic transition in the benzopyran component of the SPP. They assumed that the mechanism of the photocolouring process consists of two stages: (1) the delocalisation of two σ electrons as a consequence of the redistribution of electron density on excitation of the electronic transition in the naphthopyran component of SP_2; (2) the change in molecular configuration.

Ring opening leads to the formation of a high-energy unstable merocyanine isomer (isomer X, see above), in which there is a partial retention of the configuration of the initial form of the SPP[12]. The authors[12] suggest that this configuration can be associated with the *cis*-isomer in which the steric repulsion is balanced by the attraction of nitrogen and oxygen atoms with unlike charges. This treatment of the photocolouring of the SPP appears to us reasonable on the whole; it has been confirmed, in particular, by the results of the study of the second stage of the process (see above).

The next stage in the development of ideas concerning the mechanism of the dissociation of the $C_{(2)}-O$ bond was reached in studies[13,18,22,25,34,35,37] in which the absorption spectra of spiropyrans and compounds modelling the indoline and benzopyran components of the SPP were investigated. Their aim was to discover in which part of the SPP molecule a particular electronic transition is localised; hypotheses were put forward concerning the electronic nature of the photochemically active transition in the SPP.

The following models of the indoline component were adopted: indole[18,22], 2-hydroxy-1,3,3-trimethyl-2-phenylindoline[13], and 1,2,3,3-tetramethylindoline[25]. Different chromenes, for example, unsubstituted 2,2-diethyl-2*H*-chromene[22], 2,2-dimethyl-2*H*-chromene, or 2,2-dimethyl-5,6-benzo-2*H*-chromene[13], and substituted chromenes[25,34,35,37] were chosen as models of the benzopyran component. Comparison of the absorption spectra of the model compounds with those of solutions of the SPP permitted the conclusion that the electronic transitions, localised mainly in the indoline component of the SPP, give rise to absorption bands in the wavelength range $\lambda < 300$ nm[13,18,22,25]; mainly the absorption bands due to the electronic transitions in the benzopyran component of the SPP are distributed in the region $\lambda > 300$ nm[13,18,25,34,35,37].

However, although the absorption spectra of the model compounds make it possible to infer in which part of the SPP the particular electronic transition is largely localised, it has been noted[18,25] that the overall absorption spectra of compounds modelling the indoline and benzopyran components of the SPP agree with the absorption spectra of the SPP only to a first approximation and the difference between the intensities of the component bands is fairly large. This result shows that in practice the electronic systems of the indoline and benzopyran components of the SPP interact[1].

The electronic transition localised in the indoline component of the SPP is a $\pi-\pi^*$ transition[15]. The following information is available about the nature of the transitions localised in the benzopyran component: in the spectrum of an SPP without substituents in the benzopyran fragment the absorption bands at 313 and 324 nm are caused by the $\pi-\pi^*$ transition[13]; following the introduction of a bromine atom in the 6′-position of the SPP, a long-wavelength absorption band appears, whose dependence on the solvent polarity is characteristic of bands due to an $n-\pi^*$ transition[22], while the extinction coefficient corresponds to a $\pi-\pi^*$ transition. The author[22] denotes this transition as follows:

$$\overset{n\text{——}\pi^*}{\underset{\text{—O—}}{}}$$

emphasising thereby the electron-donating role in the latter of the oxygen heteroatom. In the SPP with a condensed benzene ring in the benzopyran component two $\pi-\pi^*$ transitions correspond to two absorption bands in the range $\lambda > 300$ nm.[13,26]

When an electron-accepting substituent, for example, the nitro-group, is introduced into the benzopyran component of the SPP, an intense absorption band appears in the range 330–360 nm, which has been ascribed to the $\pi-\pi^*$ transition[13,18,25,34,35,37]. It has been noted[22] that this band masks the absorption band due to the transition

$$\overset{n\text{——}\pi^*}{\underset{\text{—O—}}{}}$$

and $n-\pi^*$ (the latter transition involves the nitro-group). It has been emphasised[13,18,25,34,35,37] that the excitation of the $\pi-\pi^*$ transition in the benzopyran component with a nitro-group as a substituent leads to an increase of the positive charge on the oxygen heteroatom in the first excited singlet state.

The PCA transition in SPP with a nitro-group has been identified[22] as a $n-\pi^*$ transition. Bearing in mind that this $\underset{\text{—O—}}{}$ transition involves charge transfer from the oxygen heteroatom to the benzene ring, the author[22] explained the observed decrease of ϕ_{AB} by a shift of the nitro-group from the 6′-position (*para*-position relative to the oxygen heteroatom) to the 7′- and 8′-positions. However, it is believed[25] that the PCA transition in SP_8 is a $\pi-\pi^*$ transition and that the long-wavelength absorption band of the initial form of the given SPP corresponds to it. One should also note that the low-lying $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states of the SPP have been assigned[25] to states involving charge transfer from the oxygen heteroatom to the benzopyran ring.

A further development and generalisation of the ideas concerning the PCA transition in the SPP has been achieved in studies[38,39] where the dependence of the electronic absorption spectra of the initial forms and the ϕ_{AB} of the spiropyrans on their structure was investigated. A study has been made[38] of the spectral-kinetic characteristics of 20 indoline SPP under identical conditions. The absorption spectra in solution in ethyl acetate of a series of spiropyrans having characteristic structures and substituents are illustrated in Fig. 1. In order to interpret them, the authors[38] analysed the available literature data for the absorption spectra of the SPP themselves and compounds with a structure similar to that of the benzopyran component of the SPP.

It follows from the results of the study of the nature of the electronic transitions in the SPP described above[13,18,25,34,35,37] and from their relation with the photochromic transformations of the SPP[12,22,25] that the long-wavelength absorption band in the spectra of the SPP with an electron-accepting substituent in the benzopyran component is associated with the electronic $\pi-\pi^*$ transition localised mainly in the benzopyran

component. The nature of the electronic transitions in the SPP can be analysed on the basis of the fact that molecules with a structure similar to that of the benzopyran component of the SPP belong to the $(\sigma\pi nl)$-type according to the orbital classification of the electronic states of organic molecules with heteroatoms[16]. In such molecules there is a possibility of electronic transitions of the type $n-\pi^*$, $\pi l-\pi^*$, and $\pi l-\pi^*\pi_n^*$ and of the states S_0, $T_{n\pi^*}$, $S_{n\pi^*}$, $T_{\pi l,\pi^*}$, $S_{\pi l,\pi^*}$, $T_{\pi l,\pi^*\pi_n^*}$, and $S_{\pi l,\pi^*\pi_n^*}$.[16] The $\pi l-\pi^*$ and $\pi l-\pi^*\pi_n^*$ transitions represent linear combinations of the one-electron transitions $\pi-\pi^*$, $l-\pi^*$, and $\pi-\pi_n^*$; in the last two transitions the electron of the l orbital of the oxygen heteroatom passes to the π^* orbital of the π system and the π electron of the π system passes to the π_n^* orbital of the electron-accepting substituent. The excitation of the $\pi l-\pi^*$ and $\pi l-\pi^*\pi_n^*$ transitions therefore leads to charge transfer from the oxygen heteroatom to the benzene ring or from the benzopyran ring to the electron-accepting substituent. Thus the $\pi l-\pi^*$ and $\pi l-\pi^*\pi_n^*$ transitions can be characterised as transitions with intramolecular charge transfer (ICT).[16]

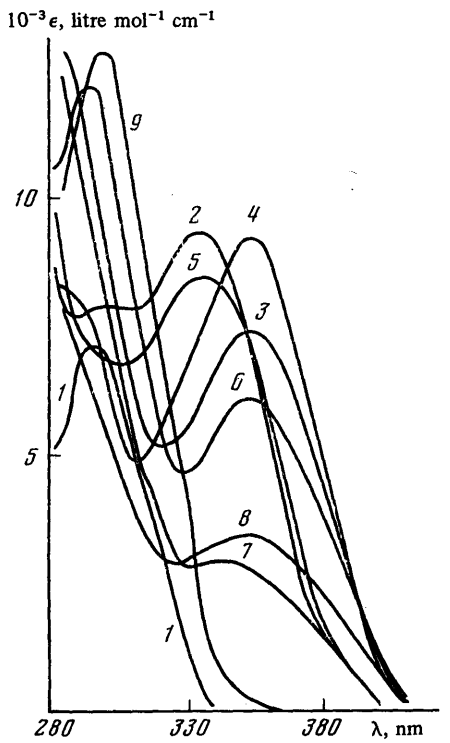


Figure 1. The absorption spectra of the initial forms of spiropyrans in solution in ethyl acetate: 1) SP_1; 2) SP_3; 3) SP_6; 4) SP_8; 5) SP_{11}; 6) SP_{17}; 7) SP_{18}; 8) SP_{20}; 9) SP_{23}.

By virtue of their specific features, the $\pi l-\pi^*$ and $\pi l-\pi^*\pi_n^*$ transitions are apparently closely related to processes which result in the dissociation of the $C_{(2)}-O$ bond; consequently, these transitions can be classified as photochemically active. In the SPP without an electron-accepting substituent in the benzopyran component the $\pi l-\pi^*$ transition must be regarded as a PCA transition. The $\pi l-\pi^*$ transition in 6'-bromo-SP_1 has been designated[22] as $n-\pi^*$. It is believed[20] that two transitions are localised in the benzopyran component of SP_1: $n-\pi^*$ and $\pi-\pi^*$ and that the $n-\pi^*$ transition is due to electron transfer from the oxygen heteroatom to the π system of the benzene ring.

On the other hand, if there is an electron-accepting substituent in the benzopyran component of the SPP, then the PCA transition is mainly of the $\pi l-\pi^*\pi_n^*$ type. The corresponding absorption band should have an intensity comparable to that of the $\pi-\pi^*$ transition band and should be located in the long-wavelength part of the absorption spectrum of the initial form of the SPP. In the absorption spectra of the SPP with a nitro-group, this band can be readily identified by comparing such spectra with the absorption spectrum of SP_1 (Fig. 1).

An important characteristic of the PCA transition is the positive charge of the oxygen heteroatom arising on excitation of this transition. It can be determined from the dipole moments of the excited and ground states of the molecule.

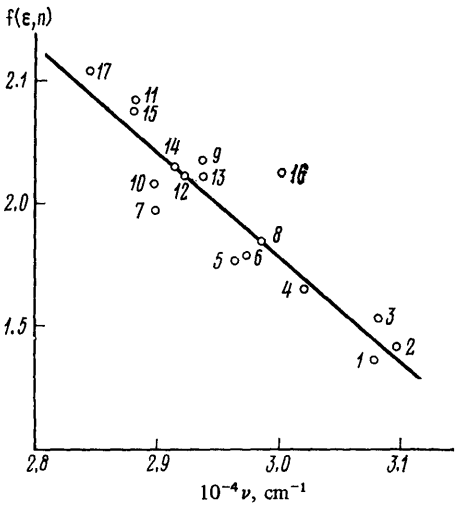
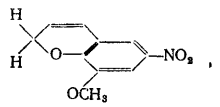


Figure 2. Dependence of the position of the long-wavelength absorption maximum of the initial form of 1,3,3-trimethyl-6'-nitrospiro[indolino-2,2'-(2'*H*-1-benzopyran)] on the universal interaction function $f(\varepsilon,n)$; solvent: 1) hexane; 2) heptane; 3) cyclohexane; 4) carbon tetrachloride; 5) benzene; 6) toluene; 7) chloroform; 8) ethyl acetate; 9) acetone; 10) dichloroethane; 11) pyridine; 12) ethyl methyl ketone; 13) dibutyl phthalate; 14) acetonitrile; 15) dimethylformamide; 16) ethanol; 17) dimethyl sulphoxide.

For quantitative estimates of the above quantities, we employed the theory of solvatochromism[40]. Fig. 2 illustrates the dependence of the shift of the ICT band of SP_3 on the universal interaction function $f(\varepsilon,n)$, which is directly related to the macroscopic characteristics of the medium—the dielectric constant ε and the refractive index n. Assuming a parallel orientation of the dipole moments of both states of the molecule, it is possible to determine the dipole moment of the molecule in the excited electronic state (μ_e)[40]

$$\mu_e = \mu_g - Chcr^3/2\mu_g \qquad (6)$$

from the slope of the linear plot of the solvatochromic shift C, the dipole moment of the molecule in the ground state μ_g, and the radius of the Onsager cavity in the solution r. Here h is the Planck constant and c the velocity of light *in vacuo*. The quantity r was assumed equal to the van der Waals radius of the molecule and was determined with the aid of X-ray diffraction data[5] ($r = 0.6$ nm for SP_3). It is known[41] that the quantity μ_g for the compound is 4.02 D. On this basis, we adopted $\mu_g = 4$ D in order to estimate μ_e for the benzopyran component of SP_8. It was found that $C = -2.2 \times 10^3$ cm^{-1}. Having substituted the selected and determined values of r, μ_g, and C in Eqn.(6), we obtain $\mu_e \cong 15$ D.



Thus the change in the dipole moment of the SP_3 molecule ($\Delta\mu$) on excitation of the photochemically active transition is ~11 D. This is in good agreement with the experimental[42] change in the dipole moment of the *p*-nitrophenol molecule in the S_0-S_1 transition, which amounts to 9 D (it is known[22] that nitrophenols constitute a fairly satisfactory model of the benzopyran component of the SPP with a nitro-group). On the basis of the value of $\Delta\mu$ and on the assumption that the dipole moment of the SP_3 molecule in the $S_{\pi l,\,\pi^*\pi_n^*}$ state arises from the unlike charges located on the oxygen heteroatom and on the nitro-group, it is possible to estimate the positive charge on the oxygen heteroatom. For a distance between the charges of 0.6 nm, the charge is found to be 0.38 e (where e is the electronic charge). This value agrees very well in its turn with the positive charge on the oxygen atom in the excited singlet state for the *t*-butyl ether of *p*-nitrophenol $(CH_3)_3C-O-Ar-NO_2$, which has been determined experimentally[43] and has been found to be 0.4 e.

It follows from the above results that the excitation of the PCA transition in the SPP does indeed lead to decreased electron density at the oxygen heteroatom in the lowest excited singlet state compared with the ground state. Since a structure of the "electron donor–Ar–electron acceptor" type, for which it is known that both the lowest excited singlet and triplet states are π,π^* states with ICT, can be identified in the benzopyran component of the SPP with an electron-accepting substituent, it appears that the $T_{\pi l,\,\pi^*\pi_n^*}$ state of the SPP with a nitro-group also involves ICT. This is supported by the finding that the lowest triplet state of the SPP is a π,π^* state (see Section III), and also by analogy with *p*-nitroaniline whose lowest triplet state has been shown[44] to be a π,π^* state with ICT.

Thus the low-lying excited singlet and triplet states of the SPP are highly polar states in which the positive charge is located on the oxygen heteroatom. An increase of the positive charge on the oxygen heteroatom leads to the polarisation of the $C_{(2)}-O$ bond and hence to its weakening. The subsequent redistribution of the electronic excitation energy among the vibrational degrees of freedom of the SPP molecule can apparently be inferred from the available data[16] concerning the mechanism of the distribution of the vibronic excitation energy in heteroatomic organic molecules.

In the study of the vibronic spectra of polyatomic organic molecules the phenomenon of the localisation of the vibronic excitation energy at specific atomic groups was observed[16]. It consists in the fact that the redistribution of energy among the vibrational degrees of freedom takes place primarily at the site of the so-called active vibrations of the molecule (these are, for example, the vibrations of the >C=O, –O–H, etc. groups). Subsequently, the energy of the active vibrations is redistributed among other vibrational degrees of freedom of the molecules of the test compound and the solvent. The active vibrations in the molecule constitute, in particular, the channels through which the selective photodissociation of the molecule takes place[16]. In the case of the SPP the active vibrations are apparently those involving the oxygen heteroatom. This hypothesis is consistent with the finding that the excitation of, for example, antisymmetric –C–O–C– vibrations leads to a higher probability of the dissociation of the $C_{(2)}-O$ bond in the excitation of any other vibrations of the SPP molecule in the excited state[13].

Thus, the mechanism of the dissociation of the $C_{(2)}-O$ bond can be represented as follows[38]: as a result of the excitation of the photochemically active transitions, localised mainly in the benzopyran component, a redistribution of electron density takes place in the SPP, which entails some increase in the positive charge on the oxygen heteroatom and the $C_{(2)}-O$ bond is polarised; in the subsequent redistribution of the electronic excitation energy among the vibrational degrees of freedom (preferentially with respect to active vibrations) the $C_{(2)}-O$ bond is ruptured. This mechanism of the dissociation of the $C_{(2)}-O$ bond can operate not only for spiropyrans but also for chromenes, which are known[13,45,46] to exhibit photochromism.

As mentioned in the introduction, the dissociation of the $C_{(2)}-O$ bond leads to the formation of an unstable configuration of the SPP molecule, i.e. the so-called X-isomer, which in the case of the SPP with an electron-accepting substituent in the benzopyran component and SP_2 has been detected by nanosecond laser photolysis at room temperature[9,10] or by low-temperature spectrophotometry[8–12]. Since the molecule in the states corresponding to the X-isomer can either return to its initial (closed) state or can give rise to the relatively stable coloured form of the SPP, it follows that ϕ_{AB} for the SPP are in the general case not greater than the quantum yield of the $C_{(2)}-O$ bond dissociation reaction [see Scheme (2)], The efficiency of the conversion of the X-isomer into the coloured form B apparently depends, like the efficiency of the dissociation of the $C_{(2)}-O$ bond, on the type and degree of the redistribution of electron density on excitation of the electronic transition in the benzopyran component of the SPP.

V. DEPENDENCE OF THE QUANTUM YIELD OF THE REACTION INVOLVING THE PHOTOCOLOURING OF SPIROPYRANS ON THEIR STRUCTURE

The ideas concerning the nature of the PCA transition, developed by two of the present authors[38,39], make it possible to explain the dependence of the efficiency of the dissociation reaction of the $C_{(2)}-O$ bond in spiropyrans on their structure. As shown in the previous Section, the PCA transition in the SPP involves intramolecular charge transfer and the corresponding absorption band can be characterised as the charge transfer band (CTB) involving charge transfer from the oxygen heteroatom to the benzopyran ring. It is known[40] that the dipole moments of transitions with ICT ($|\mathbf{D}|$) are correlated with the changes in the molecular dipole moment in the transition, i.e. the following relation holds[40]:

$$|\mathbf{D}| \sim |\Delta\mu|. \qquad (7)$$

Since the quantity $|\mathbf{D}|$ characterises the probability of the electronic transition and can be determined from the intensity of the absorption band corresponding to the given transition, it follows that, by virtue of Eqns.(7), it is possible to compare the intensity of the long-wavelength absorption band of the initial form of the SPP with the positive charge on the oxygen heteroatom and hence with the efficiency of the SPP photocolouring reaction.

In order to discover the relation between the intensity of the long-wavelength absorption band of the initial form of the SPP and their structure, one may resort to the available data for the dependence of the CTB intensity on the structure of aromatic compounds with electron-accepting substituents.

1. The addition of an electron-accepting substituent (NO_2, CHO, etc.) to an aromatic system leads to the appearance of an absorption band corresponding to charge transfer from the aromatic ring or from an electron-donating group conjugated with it to an electron-accepting substituent[16,47].

2. The CTB in the spectra of aromatic compounds with a nitro-group correspond to a transition which is polarised along the $C-N_{nitro}$ bond[47,48].

3. The intensity of the CTB depends on the degree of conjugation of the electron orbitals of the electron-donating and electron-accepting groups with the π system of the aromatic rings[16]. The degree of conjugation of the nitro-group with the π system of the aromatic rings can vary as a function of the steric and electronic (mesomeric and inductive) effects of other substituents[40,47,49]; the angle θ between the plane of the nitro-group and that of the aromatic rings can vary correspondingly[47,49].

4. The absorption spectra of *o*- and *m*-nitrophenols are similar and differ significantly from the absorption spectrum of *p*-nitrophenol[40,50]—their CTB have undergone a bathochromic shift[50,51].

5. The presence of two electron-donating substituents and one electron-accepting substituent or of one electron-donating substituent and two electron-accepting substituents in a polysubstituted benzene leads to the appearance in the absorption spectrum of a CTB which represents a superposition of the CTB of the two electron-donating groups so that of the one electron-accepting substituent or of the CTB of the single electron-donating substituent on that of the two-electron-accepting substituents[50,52].

Using the data presented, we shall attempt to explain the variation of ϕ_{AB} for the SPP (see Table) as a function of the wavelength of the exciting light and the SPP structure. In the first place one should note that in weakly polar and non-polar solvents the quantity ϕ_{AB} reaches a maximum value following irradiation of nitro-substituted SPP by light at wavelengths of 365 and 405 nm, which excite mainly the $\pi l-\pi^*\pi_n^*$ transition ($\phi_{AB}^{405} = 0.45$ for SP_8 in ethyl acetate at 293 K[38]). The values of ϕ_{AB}^{313} are lower than the corresponding ϕ_{AB}^{365} (see Table). The lower value of ϕ_{AB}^{313} compared with ϕ_{AB}^{365} can apparently be caused by the fact that the light with $\lambda = 313$ nm excites the $\pi-\pi^*$ transition in the indoline component of the SPP in addition to the $\pi l-\pi^*\pi_n^*$ transition. On the other hand, the excitation of the indoline component of the SPP can lead to the dissipation of energy through the conformational vibrations of the indoline component[22] and hence to a decrease of ϕ_{AB} for the SPP. Furthermore, the lower value of ϕ_{AB}^{313} for nitro-substituted SPP compared with ϕ_{AB}^{365} can be explained by the fact that the light with $\lambda = 313$ nm begins to excite in the benzopyran component of the SPP a transition with an energy greater than that of the PCA transition. The $C_{(2)}-O$ bond dissociation will occur at vibrational levels lying above the electronically excited states. This is indicated, for example, by the strong competition of the photochemical processes with internal conversion to the S_2 states of chromenes and SP_2,[13] as well as the formation of coloured forms of SP_3[9,22] and 6′-methoxy-SP_1[9] under the influence of light at wavelengths of 254 nm[22] and 265 nm[9-22]—this light can excite the S_0-S_3 transition in the benzopyran component of the SPP[25]. However, the excitation of these transitions, which are not photochemically active, does not apparently entail a redistribution of the electron density in the molecule necessary for the stabilisation of form B, and the efficiency of the formation of the coloured form of the SPP from the S_2 and S_3 states is therefore lower than the efficiency of their formation from the S_1 PCA state. This can explain the lower value of ϕ_{AB}^{265} compared with ϕ_{AB}^{365} for SP_3 in petroleum ether[22]. However, unambiguous conclusions are difficult to arrive at, because, as stated in Section I, the indoline fragment of the molecule absorbs in this region, which complicates the interpretation of the results.

As regards SP_2, the PCA transition in the naphthopyran component can only be the $\pi l-\pi^*$ ($2p_z-\pi^*$)[15] transition and its relative contribution to the excitation of the naphthopyran component is smaller than the contribution of the corresponding transition to the excitation of the benzopyran component in view of the more extensive π system in the former case[16]. Light at wavelengths of 313 and 365 nm therefore excites mainly the $\pi-\pi^*$ transitions in the naphthopyran component[13]. These causes also apparently account for the decrease of the values of ϕ_{AB}^{313} and ϕ_{AB}^{365} for SP_2 compared with the corresponding values for the nitro-substituted SPP and ϕ_{AB}^{313} for SP_1 (see Table).

Since the intensity of the $n-\pi^*$ transitions is lower by ~1–2 orders of magnitude than the intensity of the $\pi-\pi^*$ transitions[36], the influence of the $n-\pi^*$ transitions on ϕ_{AB} can be appreciable only in the "tail" of the band corresponding to the PCA transition. Probably for this reason the quantity ϕ_{AB}^{365} for SP_{23} is significantly smaller than ϕ_{AB}^{313}. Indeed the frequency of the $n-\pi^*$ transition, due to the CHO group, is independent of the size of the aromatic π system and amounts to 27000 cm^{-1} (370 nm)[53] and the extinction coefficient at the maximum of the band due to the $n-\pi^*$ transition is 50–60 litre $mole^{-1}$ cm^{-1} for benzaldehyde[47], i.e. amounts to half the extinction coefficient for SP_{23} at 365 nm. On the other hand, light with $\lambda = 313$ nm excites mainly the PCA transition in SP_{23} and the value of ϕ_{AB}^{313} for SP_{23} is therefore comparable to ϕ_{AB}^{313} for the SPP of the type of SP_3 (see Table) and Fig.1.

Thus, in relation to the SPP of different structures, it is seen that the successful formation of the coloured form of the SPP under the influence of light requires the excitation of a PCA transition of the type of $\pi l-\pi^*\pi_n^*$.

The variation of ϕ_{AB}^{365} over the series of nitro-substituted SPP can be accounted for by employing the known relations governing the variation of the intensity of CTB in the spectra of aromatic compounds with their structures, which are also presented at the beginning of this Section. Taking these data into account, we shall divide all the nitro-substituted SPP without condensed rings in the indoline part of the molecule into two groups. The first group includes the SPP in the benzopyran component of which it is possible to distinguish a structure corresponding to a substituted *p*-nitrophenol (see Table, SP_3-SP_{16}). The second group includes the SPP whose benzopyran components can be modelled by substituted *m*- and *o*-nitrophenols ($SP_{17}-SP_{20}$). According to the data presented above, the greatest intensity of the band dissociated with charge transfer from the oxygen heteroatom to the nitro-group will occur in the spectra of the SPP of the first group; this is confirmed by the absorption spectra illustrated in Fig.1. Accordingly, the quantity ϕ_{AB}^{365} for this group of compounds is greater than the corresponding quantum yield for the second group.

The variation of ϕ_{AB}^{365} within the groups can also be explained on the basis of the considerations described above. For example, the introduction of the OCH_3 group in the 8′-position (SP_8, SP_9) should reduce the probability of the ICT from the oxygen heteroatom to the nitro-group and hence to a decrease of ϕ_{AB}^{365} compared with ϕ_{AB}^{365} for SP_3, because there is a possibility of a competing charge transfer from the electron-donating OCH_3 group to the nitro-group. Apart from this factor, which leads to a decrease of ϕ_{AB}^{365}, when the OCH_3 or OC_3H_7 group is introduced into the 7′-position (SP_5, SP_6, and SP_7), the steric effect of the substituents will be manifested, leading to the rotation of the nitro-group relative to the plane of the benzene ring and hence to a decrease of the intensity of the PCA transition and the associated band, i.e. to an additional decrease of ϕ_{AB}^{365} (see Fig.1 and Table).

The introduction into the 8′-position of substituents with a weak electronic effect should not influence appreciably the CTB. The insignificant difference between the CTB for SP_{11} and SP_3 (Fig.1) as well as the insignificant decrease of ϕ_{AB}^{365} for SP_{11}, SP_{12}, and SP_{13} compared with ϕ_{AB}^{365} for SP_3 (see Table) are consistent with this. The appreciable decrease of ϕ_{AB}^{365} for SP_{14} following the introduction of a bromine atom in the 8′-position compared with ϕ_{AB}^{365} for SP_3 is apparently caused by the influence of the heavy bromine atom.

The presence of the heavy atom is known[54,55] to be capable of influencing the efficiency of both the intercombination transition and of the non-radiative deactivation of the triplet states of the molecule. The bathochromic shift of the long-wavelength CTB after the introduction in the 7′- or 8′-position of substituents with an appreciable electronic effect is consistent with the available data (see above).

The decrease of ϕ_{AB}^{365} for SP_{20} by a factor greater than 2 compared with that for SP_{18} in conjunction with the small difference between the intensities of the CTB in the spectra of these spiropyrans (Fig.1) may be associated with the fact that in the case of SP_{20} the band associated with the charge transfer from the oxygen heteroatom to the nitro-group is overlapped by the band associated with the charge transfer from the chlorine atom to the nitro-group.

According to X-ray diffraction data for the SP_{18} single crystal[5], the angle θ (see above) in this SPP is 54°. Since the extinction coefficient at the maximum of the band due to the charge transfer from the aromatic rings to the nitro-group is proportional to $\cos^2\theta$,[47,49] it follows that the angle θ for SP_3 can be estimated from θ for SP_{18} and the extinction coefficients at the CTB maxima for SP_3 and SP_{18}. The estimate yields a value of θ close to zero. This result is consistent with the available data for the influence of various substituents in nitrobenzene[47,49] on θ. In particular, in the absence of substituents the angle θ in nitrobenzene is zero and the band associated with the charge transfer from the benzene ring to the nitro-group has its maximum intensity[47,49]. The decrease of ϕ_{AB}^{365} for SP_{16} in dioxan almost by a factor of two compared with ϕ_{AB}^{365} for SP_8 is apparently caused by the mutual steric influence of the nitro-groups in the 5′- and 6′-positions.

The decrease of the values of ϕ_{AB}^{365} for SP_{21} and SP_{22} by more than an order of magnitude compared with ϕ_{AB}^{365} for SP_3 is probably caused by the fact that, when the benzene ring is condensed with the indoline component, the energy levels of the latter are lowered so much that, firstly, this component begins to absorb light with $\lambda = 365$ nm (i.e. the situation observed on irradiation of SPP of the type of SP_3 with light at $\lambda = 313$ nm obtains) and, secondly, the deactivation of the excited states of the benzopyran component by energy transfer to the indoline component becomes possible.

Thus the satisfactory correlation between the ϕ_{AB} for the SPP and the intensity of the long-wavelength absorption band in their spectra as a function of their structure indicates the validity of the identification[38,39] of the long-wavelength absorption band of the initial form of the SPP with the CTB band due to a PCA transition of the type of $\pi l - \pi^*\pi_n^*$ and the validity of the mechanism of the SPP photocolouring reaction based on this finding.

VI. THE MECHANISM OF THE RADIATION-INDUCED COLOURING OF SPIROPYRANS

The first studies on the radiolysis of spiropyrans in frozen solutions were carried out by Hirshberg[56,57], who established that the coloured form of the SPP produced on irradiation with fast electrons is identical with form B, which arises when the SPP is irradiated with ultraviolet light[56]. Further studies of the radiolysis of the SPP in polymers [in polystyrene, poly(methyl methacrylate), polyvinylcarbazole[22,29,39,58]] and benzene solution[7,59,60] showed that the colouring of the SPP on radiolysis takes place mainly as a result of electronic energy transfer from the matrix to the SPP via a triplet–triplet mechanism.

This result permits the conclusion that the colouring of the SPP on radiolysis proceeds mainly via the chemically active triplet state which has been shown in Section IV to be the $T_{\pi l,\,\pi^*\pi_n^*}$ state. Thus the intramolecular dissociation of the $C_{(2)}$–O bond and the formation of the coloured form of the SPP on radiolysis should in essence be of the same type as in the photoexcitation of the SPP and its efficiency should therefore be greater the more effective the population of the chemically active SPP state. This hypothesis is supported by the finding that the variation of the radiation yield of the coloured forms of the SPP (G_B) under the influence of γ-rays at 77 K proved to be similar to the analogous variation of ϕ_{AB} for the SPP (see Table). Consequently, the dependence of the efficiency of the radiation-induced colouring of the SPP on their structure can apparently be explained in terms of the ideas developed in Sections IV and V.

Indeed, it follows from a comparison of the absorption spectra of the initial forms of the SPP in polystyrene (Fig.3) that there is a correlation between the intensity of the CTB and the radiation yield of form B of spiropyrans analogous to the correlation between the intensity of the CTB in the spectrum of a solution in ethyl acetate and the radiation yield of the photocolouring process (G_B).

The influence of substituents on the efficiency of the population of the chemically active triplet state of the SPP on radiolysis can be traced in relation to SP_8. As stated in Section V, apart from the chemically active transition with charge transfer from the oxygen heteroatom to the nitro-group ($\pi l - \pi^*\pi_n^*$ transition), in this SPP there is a possibility of an analogous transition with charge transfer from the electron-donating OCH_3 group to the nitro-group ($\pi l' - \pi^*\pi_n^*$ transition), associated with a band which should undergo a bathochromic shift relative to that of the $\pi l - \pi^*\pi_n^*$ transition. The absorption spectra of the SPP presented in Fig.1 shows that the shift can be by ~2000 cm^{-1}. Since the $\pi l - \pi^*\pi_n^*$ and $\pi l' - \pi^*\pi_n^*$ transitions are of the same electronic type, presumably the $S_1 - T_0$ splittings for these transitions are likewise similar[15,16,36]. Then the sequence of the lowest electronic levels for SP_8 is as follows: S_0, $T_{\pi l',\,\pi^*\pi_n^*}$, $T_{\pi l,\,\pi^*\pi_n^*}$, etc. This sequence of triplet levels leads to an effective

deactivation of the chemically active $T_{\pi l,\,\pi^*\pi_n^*}$ level and hence to an appreciable decrease of G_B for SP_8 compared with G_B for SP_3. Indeed our estimates of the radiation yields of forms B showed that G_B for SP_8 is almost an order of magnitude smaller than for SP_3 (see Table).

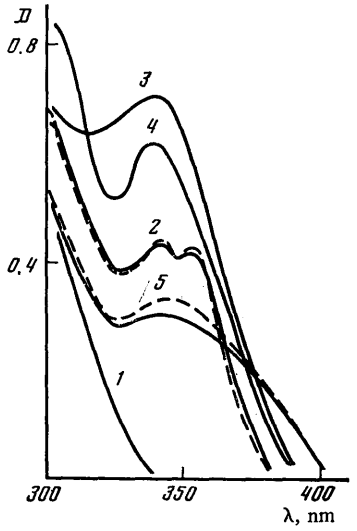
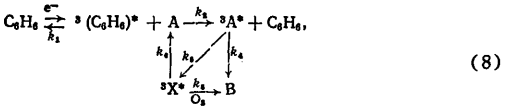


Figure 3. Absorption spectra of polystyrene films of identical thickness with added spiropyrans at equal concentrations at room temperature (continuous lines) and at 77 K (dashed lines): 1) SP_1; 2) SP_2; 3) SP_3; 4) SP_4; 5) SP_{18}.

Analogous results for the dependence of the efficiency of the radiation-induced colouring of the SPP on their structure were obtained in a study of the pulse radiolysis of benzene solutions of indoline SPP (compounds SP_3^*, SP_8^*, and SP_{14}^*), having benzopyran components similar to those of SP_3, SP_8, and SP_{14} respectively[7,58,59,60]. Kryukov and Vannikov[60] published a mechanism of the colouring of the SPP on radiolysis:



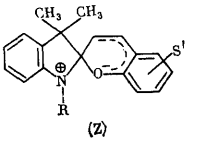
(8)

where $^3X^*$ is the triplet state of the X-isomer of the SPP. The rate constants for the formation of form B in a solution through which helium is bubbled have the following values (s^{-1}): $k_4 \geq 10^8$ and $k_8 \cong 10^4$, while in the presence of oxygen we have $k_4 \geq 10^8$ and $k_8 \cong 1.5 \times 10^6$.[59,60] It has been noted[59,60] that the ratio of the rapid and slow stages in the formation of form B depends greatly on the SPP structure. For example, the ratio of the optical densities of form B at the maximum of its long-wavelength absorption band $D^1_{\lambda max}/D^2_{\lambda max}$ ($D^1_{\lambda max}$ was measured immediately after a 40 ns pulse and $D^2_{\lambda max}$ was measured after 1 μs) is 0.6 for SP_3^*, 0.3 for SP_{14}^*, and 0 for SP_8.[60] The absence of a rapid stage in the reaction involving the formation of form B for SP_8 can be explained by the fact that the chemically active $T_{\pi l,\,\pi^*\pi_n^*}$ ($^3A^*$) state is effectively deactivated as a consequence of the internal transition to the $T_{\pi l',\,\pi^*\pi_n^*}$ state, which is chemically inactive.

It has been noted[60] that the method of pulse radiolysis is preferable for the investigation of the mechanism of the formation of the coloured form of the SPP from the triplet states of the initial form of the SPP compared with the method of sensitised photocolouring of the SPP in view of the fact that the introduction of high concentrations of triplet energy donors introduces an uncertainty into the interpretation of the processes occurring in the system.

A short-lived absorption band in the region of 450 nm has been discovered[59] and assigned to the triplet–triplet transition of the intermediate, which is a *cis*-cisoid isomer of the SPP (X-isomer) in the triplet state. At the same time the ground state of the X-isomer was not manifested optically in the wavelength range from 450 to 650 nm[59] (the absorption band due to the S_0–S_1 transition of the X-isomer is in the range 440–460 nm[6,9–11]).

The establishment of the triplet states of the initial forms of the SPP in the photolysis of single crystals of nitro-substituted SPP at low temperatures has been observed[61,62] by EPR. The author[61] attributed the observed EPR signals to the EPR spectrum of a radical pair with an average distance between the paramagnetic centres of 0.26 nm. It has been suggested[29,61] that the radical pairs are formed as a result of an intramolecular electron phototransfer from the indoline component of the SPP to its benzopyran component and can be represented schematically as follows:



(Z) (9)

The distance between the nitrogen and oxygen heteroatoms of the indoline and benzopyran components, determined by X-ray diffraction[5], is 2.3 Å. Bearing in mind that the difference between this quantity and the average distance between the paramagnetic centres in a triplet radical pair can be due to the steric delocalisation of the interacting electrons and the inaccuracy of the description of their interaction by the point dipole moment[63], it appears that the mechanism of the formation of these pairs proposed by the present authors[29] does indeed operate. It is noteworthy that it has also been suggested[15,29] that the intermediate Z is involved in the photocolouring of the SPP. We may point out that generally speaking the triplet state of the X-isomer, to the triplet–triplet absorption of which a short-lived band at 450 nm has been ascribed[59,60], may be similar to Z in its nature.

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