

# Photochemistry of a 6'-cyanosubstituted spironaphthooxazine: photo-induced decay of an open form

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**Photochemistry of three 6'-cyanosubstituted spironaphthooxazines (SNO) in ethanol matrices at 77 K was studied by means of ultraviolet (UV) and erythrocyte sedimentation rate (ESR) spectroscopy and quantum chemistry. The quantum yield of the open form photolysis is found to be 0.01–0.02, which is high enough for 77 K. For one of the SNO, the formation of a merocyanine form radical was observed. The radicals were formed by an H atom abstraction from the solvent molecule to the light-excited merocyanine isomers. The formation of a merocyanine radical represents a new specific channel of photochemically induced degradation of spirooxazines. Copyright © 2011 John Wiley & Sons, Ltd.**

**Keywords:** frozen matrices; photochemistry; photochromism; quantum chemistry; spirooxazines

## INTRODUCTION

Spirooxazines represent one of the most important classes of organic photochromic compounds.<sup>[1–3]</sup> Firstly, they demonstrate very high molar absorptivity of colored form.<sup>[1–4]</sup> Secondly, spirooxazines are more stable to the processes of photochemical degradation in comparison with structurally similar spiropyrans.<sup>[2]</sup>

Photochromic properties of spirooxazines are caused by mutual transitions between colorless spiro-form A and colored merocyanine form B (Scheme 1 demonstrates these transitions for 6'-cyanosubstituted spironaphthooxazines, further SNO). In the closed form indoline and oxazine moieties of the molecule are perpendicular to each other and do not form conjugated bonds. In the merocyanine form, the molecule has almost flat geometry and a common conjugated  $\pi$ -electronic system. In accordance with the structure, the closed form demonstrates absorption only in the ultraviolet (UV) spectral region, and the open form has a very intense (molar extinction coefficient exceeds  $5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) absorption in the visible spectral region. As a role, irradiation of spirooxazines in the UV region results in blue coloration due to photochemical reaction  $A \rightarrow B$ . The backward reaction  $B \rightarrow A$  can occur both thermally and photochemically.

Mechanism of photochromic reactions of spirooxazines was studied in liquid solutions by means of stationary<sup>[5–7]</sup> and laser flash photolysis with nano-,<sup>[8–10]</sup> pico-,<sup>[11–13]</sup> and femto-second<sup>[14–16]</sup> time resolution. Typically it is assumed<sup>[17]</sup> that absorption of a light quantum by a closed form of spirooxazine (or spiropyran) leads to the cleavage of the bond between spiro atom of carbon and atom of oxygen, but the planes of the molecular moieties still remain perpendicular. The

resulted intermediate proposed by Fisher *et al.*<sup>[18,19]</sup> is called X-isomer. Mutual rotation of the two molecular moieties results in transition of X-isomer to the flat structure of the merocyanine form. In ultrafast kinetic spectroscopy experiments, intermediates absorbing in the region of 400–500 nm were observed for both spiropyrans<sup>[20]</sup> and spirooxazines.<sup>[21]</sup> These intermediates were interpreted as X-isomer. Typical lifetimes of X-isomer in common solvents are in the range of 1–30 ps, coinciding with the characteristic time of merocyanine isomer formation.

The mechanism of photochromic transformation could depend on the structure of the spirocompounds. Besides the formation of an open form via X-isomer  $A \rightarrow X \rightarrow B$ , another reaction pathways are discussed in the literature. These are:

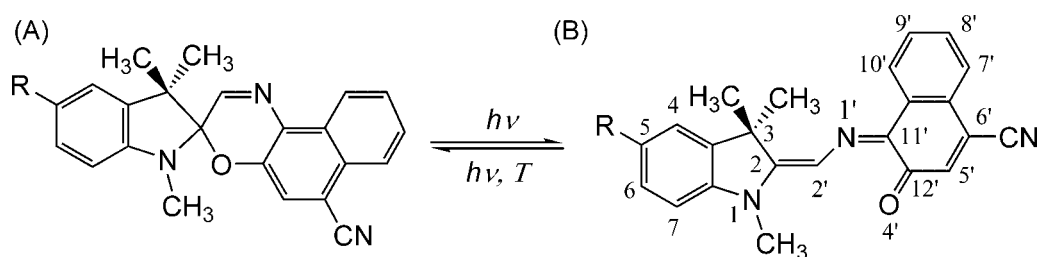
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**Scheme 1.** Closed (spiro-form, A-form) and open (merocyanine form, B-form) of 6'-cyanosubstituted spironaphthooxazines

- $A \rightarrow X^* \rightarrow B$ , in which X-isomer exists only in the excited state;<sup>[14]</sup>
- $A(S_0) \rightarrow A(S_1) \rightarrow B$ , when isomers of B-form occur directly from a singlet excited state of A-form, without X-isomer formation;<sup>[22]</sup>
- different pathways involving triplet state of A-form.<sup>[17,23–25]</sup>

In addition to time-resolved methods, information on the mechanisms of photochromic transformations could be obtained from the experiments at low temperature, e.g. in frozen matrices<sup>[18,19,26–28]</sup> and polymeric films.<sup>[29–31]</sup> In this case one can expect an increase in the lifetimes of intermediates. Thus, in Reference<sup>[28]</sup> the laser flash photolysis of phenanthroline-containing spirooxazines in methanol glasses (77 K) was performed. An intermediate transforming into the B-form with the characteristic lifetime of several microseconds was registered. This intermediate was interpreted as an X-isomer. For one of the compounds studied in Reference<sup>[28]</sup> a partial stabilization of an X-isomer at 77 K was assumed.

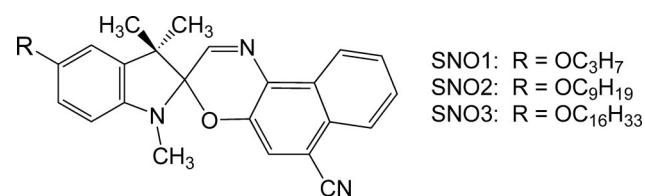
In the current work the photochemistry of three previously synthesized<sup>[32,33]</sup> SNO in frozen organic matrices (77 K) was studied. The main goal was to examine the possibility of X-isomer stabilization at 77 K. This effect was not found. Instead, a new photochemical reaction of an open form leading to the degradation of a spirooxazine was observed.

## EXPERIMENTAL

Photochemistry of three SNO (further – SNO1, SNO2, and SNO3) with different substituents in the fifth position of the indoline moiety (Scheme 2) was studied. The synthesis of SNO is described in the work.<sup>[33]</sup>

Chemically pure ethanol additionally purified by fractional distillation was used for preparation of solvents and low-temperature matrices. For calculations of SNO concentrations in solid matrices, the coefficient of volume compression (0.82 at 77 K) was taken into account.

Stationary photolysis was performed by a high pressure mercury lamp with a set of colored glass filters (LOMO,



**Scheme 2.** Studied SNO (A-form)

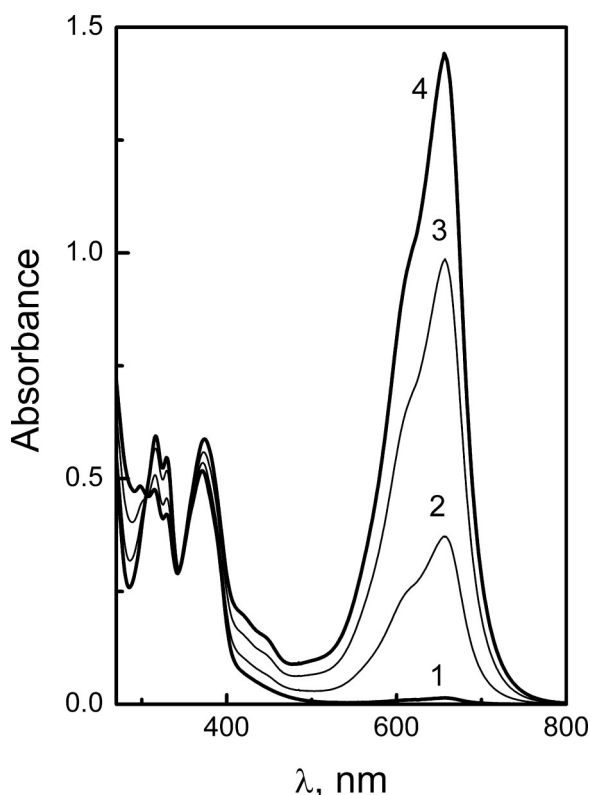
Saint Petersburg, Russia) for separating necessary wavelength of irradiation. UV spectra were recorded using Agilent 8453 spectrophotometer (Agilent Technologies). Electron spin resonance (ESR) spectra were recorded using ESR-300 spectrometer (Bruker). Concentration of free radicals in the samples was determined by integration of ESR spectra and calibration using a  $\text{CuCl}_2 \times 2\text{H}_2\text{O}$  single crystal as a standard. The simulations of ESR spectra were performed with the Winsim v1.0 program.

The procedure of low-temperature photochemical experiment is described in details elsewhere.<sup>[34]</sup> To compare quantitatively the data obtained by the methods of UV and ESR spectroscopy, the corresponding spectra were recorded using the same sample.<sup>[34]</sup> Ferrioxalate actinometer<sup>[35]</sup> was used to measure light intensity for calculations of quantum yields.

## RESULTS AND DISCUSSION

### Photolysis of SNO at 300 and 77 K

Typically spirooxazines exist in solutions as an equilibrium mixture of closed and open forms.<sup>[36]</sup> In the case of SNO the percentage of an open form in equilibrium does not exceed 0.3%. Therefore, its absorption in the visible spectral region is negligible. Irradiation of a closed form of SNO in the near-UV spectral region leads to the formation of an open form. Figure 1 shows the spectral changes of SNO3 (in ethanol solution) in the course of photolysis. The formation of an intense band of the merocyanine form in the region of 600 nm is observed. The prolonged irradiation results in the formation of a photostationary state due to balance between forward ( $A \rightarrow B$ ) and backward ( $B \rightarrow A$ ) photochemical reactions. When irradiation is stopped, the thermal backward reaction  $B \rightarrow A$  leads to the bleaching of the solutions. The kinetic curves of thermal bleaching are satisfactorily fitted by exponential curves. Spectral, photochemical, and kinetic parameters for SNO in ethanol solutions at 300 K are collected in Table 1. Quantum yields of direct photolysis in ethanol  $\varphi_{AB}$  are about 0.05. This is 2.5 times lower than the values of quantum yields in toluene measured for these compounds in Reference<sup>[33]</sup>. The values of  $\varphi_{AB}$  in toluene and methanol for another SNO (with  $R = \text{OCH}_3$ ) measured in Reference<sup>[33]</sup> were 0.11 and 0.05 correspondingly. The typical values of quantum yields for spirooxazines fall within the range 0.1–0.5 and could demonstrate strong solvent dependence.<sup>[3]</sup> For the majority of spirooxazines mentioned in the review<sup>[3]</sup> the values of quantum yield in polar solvents (alcohols) are 2–3 times lower than in toluene and methylcyclohexane, but this is not obligatory. Therefore, for SNO1, SNO2 and SNO3 the values of  $\varphi_{AB}$  are about lowest among spirooxazines family, and the



**Figure 1.** Changes in the UV spectrum of SNO3 ( $7.3 \times 10^{-4} \text{ mol L}^{-1}$  in 1 cm cell) under the irradiation (365 nm) in EtOH at 300 K. Curves 1–4 correspond to 0, 7, 25, 55 s of irradiation

ratios of quantum yields in polar and non-polar solvents are typical.

The near-UV irradiation of SNO in frozen ethanol matrices at 77 K also leads to the formation of an open form. The maximum of the B-form absorption band in frozen matrix is *ca.* 30 nm shifted to the blue side of the spectrum. This fact is explained by the transitions between the isomers of an open form.<sup>[37]</sup>

The quantum yield at 77 K drops in a factor of 3–4 in comparison with the process performed at 300 K. Spectral and photochemical properties of SNO in frozen ethanol matrices

(77 K) are collected in Table 2. The details of low-temperature experiments are reported in Reference<sup>[37]</sup>.

The prolonged irradiation of SNO1 and SNO2 in frozen ethanol matrices leads to establishing of a photostationary state, like in the case of the photolysis in liquid solutions. No new absorption bands occur in this case. On the contrary, the prolonged irradiation of SNO3 in a frozen ethanol matrix results in the formation of a new and unexpected product.

#### Peculiarities of SNO3 photolysis at 77 K

The dramatic changes in the UV spectrum of SNO3 in ethanol matrix (77 K) caused by the irradiation in the region of 365 nm are shown in Fig. 2. Two stages of photolysis are clearly observed. At the first stage the absorption band with a maximum at 650 nm is formed. This band definitely belongs to an open (merocyanine) form of SNO3. In a course of irradiation, the formation of the merocyanine absorption band terminates, and a new band with its maximum at 540 nm occurs. This band was not observed in the photolysis of SNO1 and SNO2, which had structures close to that of SNO3. Dissolved oxygen was not found to affect the formation of this band.

The new band seems to yield by the photolysis of the merocyanine form. This suggestion is supported by the experiment on the direct photolysis of the B-form (Fig. 3). The merocyanine form was accumulated by the photolysis of a closed form at 300 K followed by the fast cooling to 77 K (curve 1 in Fig. 3). Note that the double peaked spectrum of B-form shown in Fig. 3 (curve 1) is different from that in Fig. 2. This fact is explained by the temperature dependence of the B-form spectrum.<sup>[37]</sup> This dependence is determined by two factors: (i) equilibrium between transoid isomers of B-form (presumably, between the most stable TTC and CTC, see item Quantum chemical calculations of SNO) and (ii) changes in extinction coefficients of individual absorption bands. These dependencies are reflected in photochemistry. The spectra of the B-form obtained by the photolysis at 77 K and by photolysis at 300 K followed by cooling to 77 K do not coincide completely.<sup>[37]</sup>

The irradiation (365 nm) of the samples reached with the open form of SNO3 results in the disappearance of the B-form band and the formation of a new absorption band with its maximum at 540 nm (curves 2–4 in Fig. 3). The conservation of an isosbestic point (at 585 nm) indicates the photochemical transition of the

**Table 1.** Spectral (maxima and molar extinction coefficients of absorption bands of A- and B-forms), kinetic (rate constants of B → A reaction), and photochemical (quantum yields of A — hv → B reaction) properties of SNO in ethanol solutions at 300 K

SNO	$\lambda_{\text{max}}^{\text{A}}$ (nm)	$\epsilon_{\text{max}}^{\text{A}} \times 10^{-3}$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	$\lambda_{\text{max}}^{\text{B}}$ (nm)	$^* \epsilon_{\text{max}}^{\text{B}} \times 10^{-4}$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	$k_{\text{BA}} \times 10^4$ ( $\text{s}^{-1}$ )	$\phi_{\text{AB}}$
SNO1	316	7.0	656	6.3	5.1	$0.053 \pm 0.003$
	327	6.6				
	370	6.3				
SNO2	316	7.7	656	6.3	4.9	$0.046 \pm 0.003$
	327	7.2				
	370	6.9				
SNO3	316	8.1	656	6.1	5.6	$0.043 \pm 0.002$
	329	7.4				
	370	7.1				

\* Measured in Reference<sup>[33]</sup>

**Table 2.** Spectral and photochemical properties of SNO in frozen ethanol matrices (77 K)

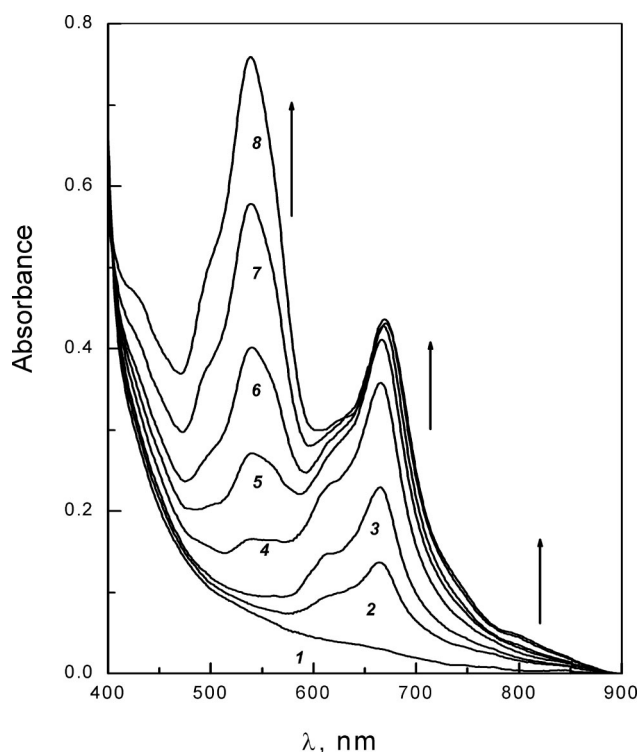
SNO	$\lambda_{\max}^A$ (nm)	$\varepsilon_{\max}^A \times 10^{-3}$ ( $M^{-1} \text{cm}^{-1}$ )	$\lambda_{\max}^B$ (nm)	$\varepsilon_{\max}^B \times 10^{-4}$ ( $M^{-1} \text{cm}^{-1}$ )	$\varphi_{AB}$
SNO1	316	8.8	622	4.8	$0.017 \pm 0.004$
	330	7.2			
	373	9.7			
SNO2	316	8.5	622	5.6	$0.019 \pm 0.005$
	328	7.4			
	371	8.7			
SNO3	319	8.8	622	6.0	$0.011 \pm 0.003$
	333	7.9			
	376	8.0			

B-form to a new product, which is called further the C-form of SNO3.

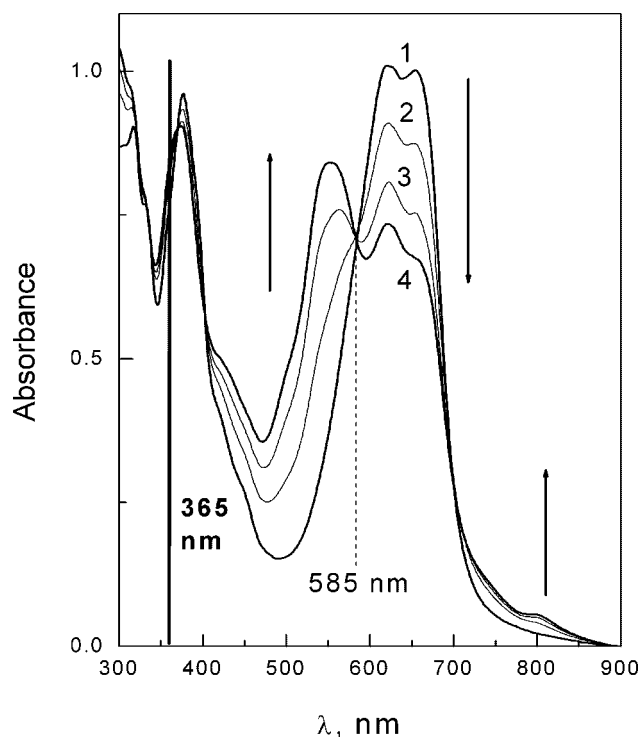
It is interesting that the irradiation of the sample containing B and C-forms in the region of 436 nm (Fig. 4) leads to the disappearance of the B-form band and does not affect the C-form band. This indicates the occurrence of B  $\rightarrow$  A photochemical reaction. The irradiation in the range of  $>500$  nm does not result in any changes in the UV spectrum. The tentative explanation of the wavelength dependence of the reaction pattern will be given below.

The conservation of the isosbestic point upon the photolysis of the B-form (Fig. 3) allows one to calculate the spectrum of the C-form using the known UV spectrum of the B-form. The spectrum of the C-form of SPO3 is shown in Fig. 5. The maximal

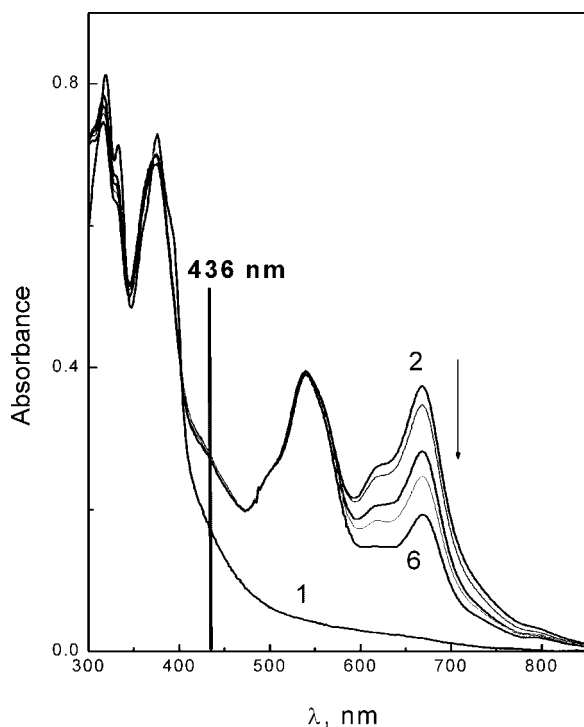
extinction coefficient of the C-form band at 540 nm ( $1 \times 10^5 M^{-1} \text{cm}^{-1}$ ) is rather high. The question to identify the nature of the C-form arises. The first hypothesis to examine was the assumption that the C-form coincides with the X-isomer of the open form. This assumption is based on the results on femtosecond spectroscopy of SNO2 in liquid toluene and polystyrene films at 300 K.<sup>[33]</sup> In this work, the intermediate absorption band with its maximum just at 540 nm and the lifetime of 2–4 ps was attributed to the X-isomer of SNO2. One can assume that X-isomers could be partially stabilized at 77 K, because the free rotation of the molecular fragments (leading to X  $\rightarrow$  B transformation) could be hampered in a low-temperature matrix. This hypothesis was put forward in Reference<sup>[28]</sup> to explain the peculiarities of the photolysis of



**Figure 2.** Photolysis (365 nm) of SNO3 ( $7.2 \times 10^{-4} \text{ mol L}^{-1}$  in 0.17 cm cell) in EtOH at 77 K. Curves 1–8 correspond to 0, 5, 20, 120, 300, 600, 1200, 2400 s of irradiation

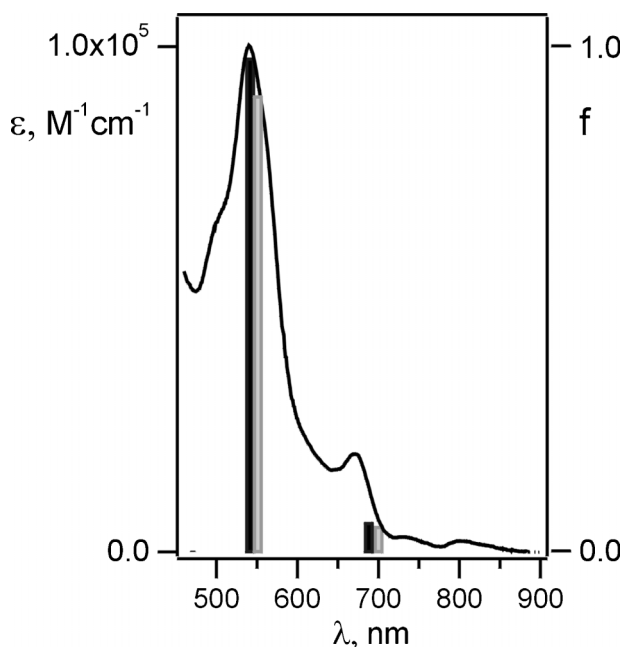


**Figure 3.** Photolysis (365 nm) of the open form of SNO3 ( $6.7 \times 10^{-4} \text{ mol L}^{-1}$  in 0.17 cm cell) in EtOH at 77 K. Open form was obtained by the irradiation of the closed form at 300 K. Curves 1–4 correspond to 0, 50, 110, 180 min of irradiation

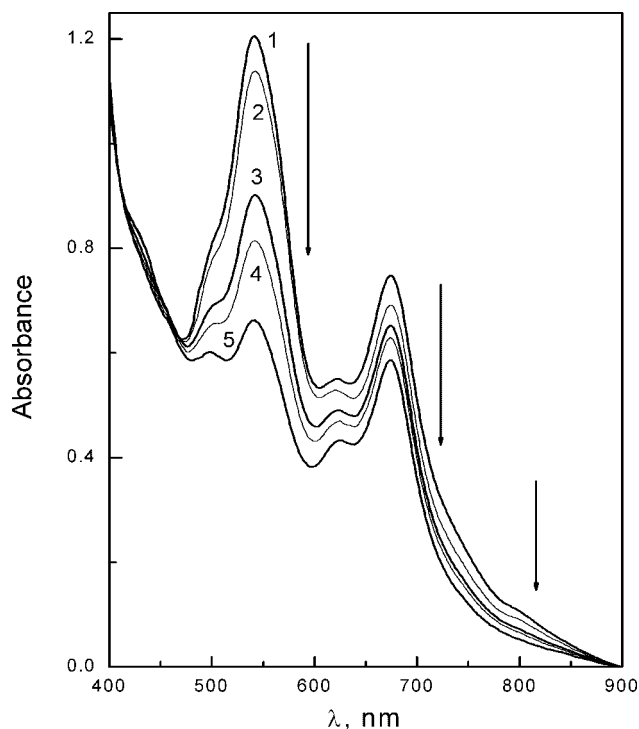


**Figure 4.** Photolysis (436 nm) of the open form of SNO3 in EtOH at 77 K ( $5.4 \times 10^{-4} \text{ mol L}^{-1}$  in 0.17 cm cell). Curve 1 – initial spectrum; curve 2 – spectrum after 60 min of irradiation at 365 nm; curves 3–6 correspond to 1, 10, 30, 140 min of irradiation at 436 nm

a phenanthroline-containing spironaphthooxazine (SPO) in a frozen matrix. Possibility of C-form coincidence with the X-isomer was examined in the experiment on the C-form annealing. If the C-form is an X-isomer, the reaction  $X \rightarrow B$  should occur in a course



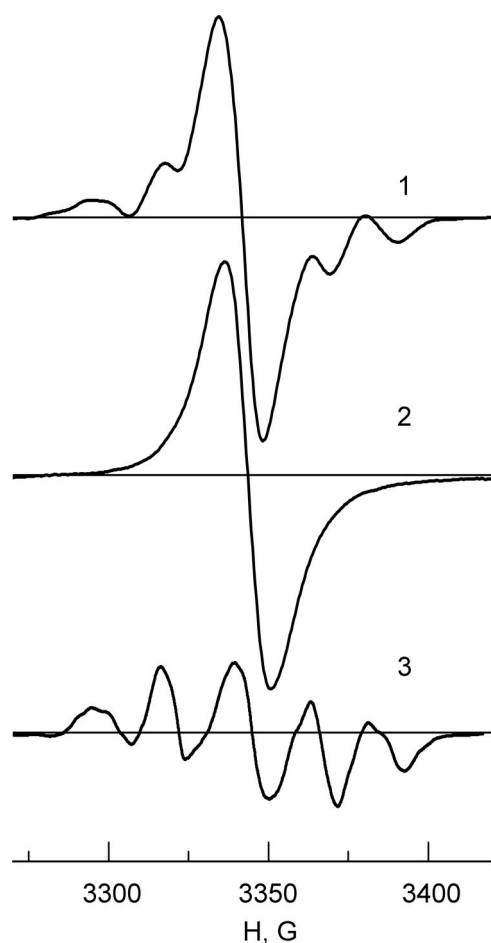
**Figure 5.** UV spectra of the final product of SNO3 photolysis at 365 nm (C-form) in EtOH at 77 K. The vertical black and gray bars indicate the positions and oscillator strengths ( $f$ ) of the electronic transitions calculated for TTCH and CTCH radicals respectively (see text)



**Figure 6.** Annealing of the product of SNO3 photolysis in EtOH ( $1.3 \times 10^{-3} \text{ mol L}^{-1}$  in 0.17 cm cell). Curve 1 – spectrum after 60 min of irradiation (365 nm). Curves 2–5 correspond to 20 min at 103 K; 30 min at 104 K; 10 min at 109 K; 45 min at 114 K. Spectra were recorded at 77 K

of annealing. Nevertheless, Fig. 6 shows that the annealing in the region of 103–114 K (which is close to the glass transition temperature of ethanol  $T_g = 116 \text{ K}^{[38]}$ ) results in the disappearance of the C-form, and no increase in the absorption of the B-form band takes place. Therefore, the C-form could not coincide with the X-isomer.

An increase in absorbance at 540 nm was found to be accompanied with the occurrence of the ESR spectrum shown in Fig. 7. No ESR signals were observed for SNO1 and SNO2 (which is in agreement with the absence of the C-form manifestation in the UV spectra). At low exposition time (curve 1) the ESR spectrum contains a quintet typical for  $\text{CH}_3\text{CHOH}$  radical<sup>[39]</sup> superimposed with a singlet at  $g \approx 2$ . For comparison, curve 3 shows the spectrum of  $\text{CH}_3\text{CHOH}$  obtained by  $\gamma$ -radiolysis of ethanol.<sup>[40]</sup> At higher exposition time (curve 2) the spectrum of  $\text{CH}_3\text{CHOH}$  radical completely disappears and the singlet at  $g \approx 2$  with the linewidth of about 15 G is an only ESR signal. The irradiation of ethanol matrix at the same conditions did not result in the formation of the ESR signal. To compare results of UV and ESR spectroscopy, the experiment on the photolysis of SNO3 with recording of the UV and ESR spectra using the same sample was performed. The number of molecules of C-form appeared in the course of photolysis was determined from the UV spectra, and the number of radical products was determined from the ESR spectra. The results are shown in Fig. 8. It is evident from Fig. 8 that C-form of SNO3 and free radicals occur in the same process. The formation of an  $\alpha$ -hydroxyethyl radical testifies that a hydrogen atom attraction from the molecule of matrix should take place. The attracted H atom seems to attach to an oxygen atom of a merocyanine form of SNO3. As a result, a radical of a merocyanine form occurs. In the framework of this conception, C-form of SNO3 is the merocyanine radical. Further it will be



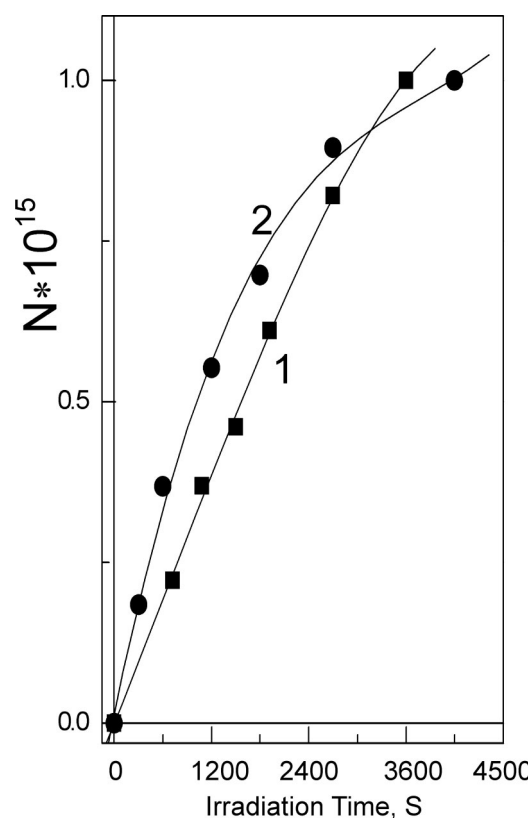
**Figure 7.** ESR spectra: (1) product of SNO<sub>3</sub> photolysis in EtOH (355 nm (YAG laser), initial stage); (2) product of deep photolysis of SNO<sub>3</sub> in EtOH (365 nm); (3) spectrum of CH<sub>3</sub>CHOH radical obtained by  $\gamma$ -radiolysis of ethanol [37]. Temperature 77 K

shown by means of quantum chemistry calculations that the mentioned radical could have both an intensive absorption band in the region of 540 nm and a singlet ESR spectrum with a linewidth of 15 G. The disappearance of merocyanine radicals in the course of annealing (Fig. 6) represents a new channel of the SNO<sub>3</sub> photodegradation.

The hydrogen atom abstraction is wavelength dependent, which is evident from the comparison of Figs 3 and 4. C-form occurs efficiently by the B-form photolysis at 365 nm (Fig. 3) and does not occur in the course of the B-form excitation at 436 nm (Fig. 4). Probably, the reason is that in the case of 436 nm photolysis the energy of light quantum is less than necessary for H atom abstraction from the molecule of matrix.

It should be noted that the complication with the explanation of the ESR signal at  $g \approx 2$  with the linewidth of 15 G exists. Besides the merocyanine radical, one should consider the products of the photolysis of  $\alpha$ -hydroxyethyl radical. Several types of radicals occur in the course of photochemical and thermal reactions. These are CH<sub>3</sub>CHOH, CH<sub>3</sub>CH<sub>2</sub>, CH<sub>3</sub>CO,  $\cdot$ CH<sub>3</sub>, and CH<sub>3</sub>C( $\cdot$ CO)HOH radicals. The main facts about behavior of these radicals in ethanol matrices known from literature are listed below:

1. Prolonged irradiation of matrices containing CH<sub>3</sub>CHOH radicals in the near UV spectral region results in the formation of CH<sub>3</sub>CH<sub>2</sub> and CH<sub>3</sub>CO radicals.<sup>[41]</sup>

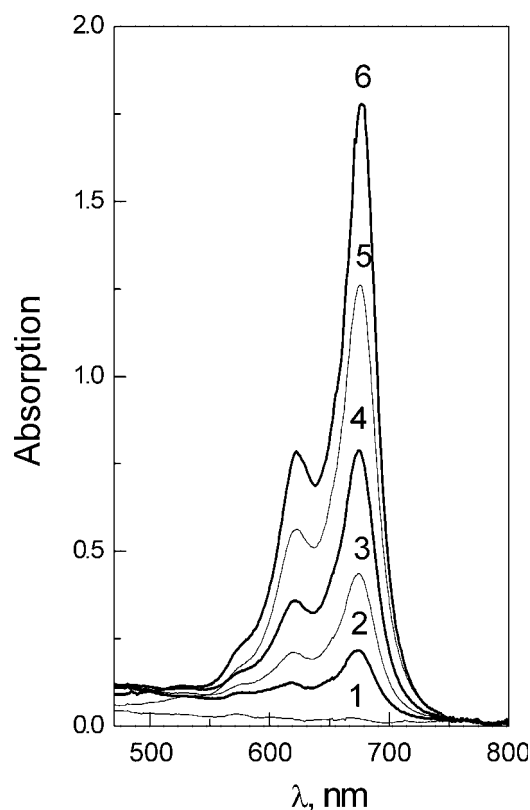


**Figure 8.** Changes in the concentrations of the final product of SNO<sub>3</sub> photolysis (monitored at 540 nm) (1) and free radicals (monitored by ESR) (2). Temperature 77 K, UV and ESR spectra were recorded using the same sample

2. CH<sub>3</sub>CH<sub>2</sub> radicals abstract H atoms from the matrix molecule with the restoration of CH<sub>3</sub>CHOH radicals.<sup>[42]</sup>
3. The ESR spectrum of the acyl radical CH<sub>3</sub>CO comprises a singlet with  $g \approx 2$  and linewidth of about 15 G.<sup>[43]</sup> CH<sub>3</sub>CO disappears under irradiation with the near UV and visible light yielding carbon monoxide and the methyl radical.<sup>[41,43]</sup>
4. The methyl radicals in ethanol matrix are transformed to the CH<sub>3</sub>CHOH radicals (in the dark reaction with the matrix molecules<sup>[44,45]</sup>).
5. Addition of CO (produced in the photolysis of the CH<sub>3</sub>CO radical) to the CH<sub>3</sub>CHOH radical results in the formation of the CH<sub>3</sub>C( $\cdot$ CO)HOH radical.<sup>[41]</sup> This is an acyl type radical, and its ESR spectrum is alike to the CH<sub>3</sub>CO radical. The CH<sub>3</sub>C( $\cdot$ CO)HOH radicals are less photochemically active than CH<sub>3</sub>CO. They are accumulated in the ethanol matrix containing  $\alpha$ -hydroxyethyl radicals under the prolonged irradiation with light in near UV and visible regions.<sup>[40,46]</sup>

By this means the transformation of the CH<sub>3</sub>CHOH radicals to the CH<sub>3</sub>C( $\cdot$ CO)HOH acyl radicals occur under the prolonged irradiation. The accumulation of the CH<sub>3</sub>C( $\cdot$ CO)HOH radicals explains the disappearance of the structure of the ESR spectrum under the prolonged irradiation (Fig. 7). Note that the final singlet ESR spectrum (curve 2 in Fig. 7) is the superposition of two alike spectra belonging to the different radicals, merocyanine radical and CH<sub>3</sub>C( $\cdot$ CO)HOH.

The key role of matrix in the formation of the C-form was examined in the experiment on the photolysis of SNO<sub>3</sub> in a Freon



**Figure 9.** Photolysis (365 nm) of SNO3 ( $2.7 \times 10^{-4} \text{ mol L}^{-1}$  in 0.17 cm cell) in  $\text{CCl}_3\text{F} + \text{C}_2\text{F}_4\text{Br}_2$  (1:1) at 77 K. Curves 1–6 correspond to 0, 10, 30, 120, 300, 2400 s of irradiation

matrix obtained by (1:1) mixing of trichlorofluoromethane and 1,2-dibromo-1,1,2,2-tetrafluoroethane. These two hydrogen free solvents form a transparent glassy matrix at 77 K. Changes of the UV spectrum of SNO3 in the course of photolysis in Freon matrix are shown in Fig. 9. Only appearance of the B-form absorption

band is observed, which does not transform to the absorption of the C-form band. ESR spectrum was not found to occur in the course of photolysis. Experiments in the Freon matrix prove that atoms of hydrogen of the solvent affect in the formation of the C-form.

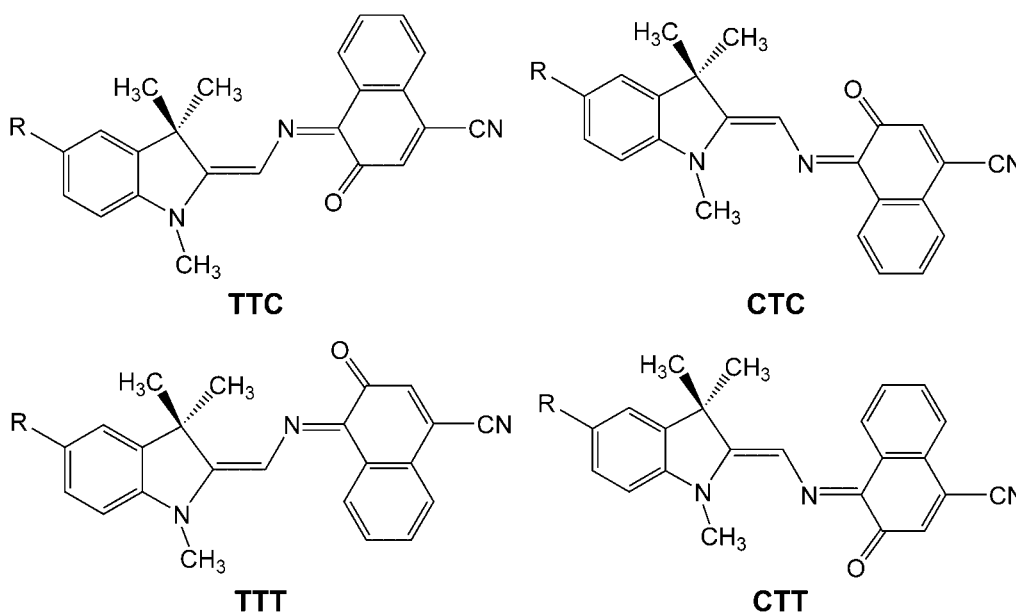
It should be noted that an alternative mechanism of the appearance of C-form could be proposed. One could assume that for SNO with the longest substituent in an indoline moiety the R chain (Scheme 2) is situated in the vicinity of an oxygen atom of the oxazine moiety. The experiments on the photolysis in hydrogen free matrices allow one to rule out this possibility.

When the photolysis of SNO3 was performed in frozen (77 K) 3-methylpentane or cyclohexane glasses, the occurrence of the C-form UV absorption and the corresponding singlet ESR spectrum were observed in the course of prolonged photolysis. The C-form yield in alkanes is much less than in the ethanol matrix.

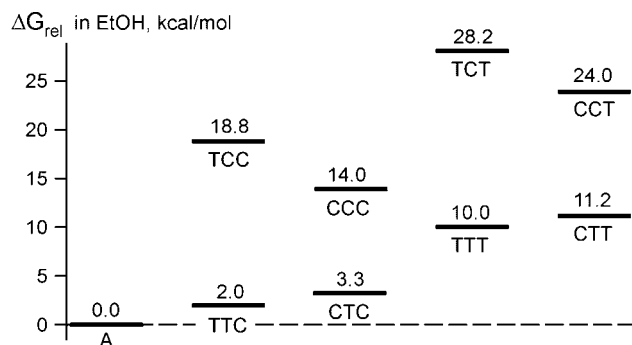
### Quantum chemical calculations of SNO

To support the results of the photolysis of SNO3, the quantum chemical calculations were performed. For calculations, the simplified structure of SNO with  $\text{R} = \text{OH}$  (Scheme 2) was used. Gibbs energies of formation were calculated for a closed form (A-form), *cis-trans* isomers of open forms (B-forms), and radicals of merocyanine (C-form) at the PBE0<sup>[47]</sup> level of theory with 6-31G(d,p) basis set, using the Gaussian-03 suite of programs.<sup>[48]</sup> The influence of the solvent on the energies of stationary points was taken into consideration by the PCM<sup>[49–51]</sup> models as implemented to Gaussian-03. To predict the electronic absorption spectra of radicals of merocyanine, the time-dependent (TD) DFT method<sup>[52–54]</sup> with the hybrid functional of Perdew, Burke, and Ernzerhof (PBE0)<sup>[48]</sup> was used with 6-31+G(d,p) basis set.

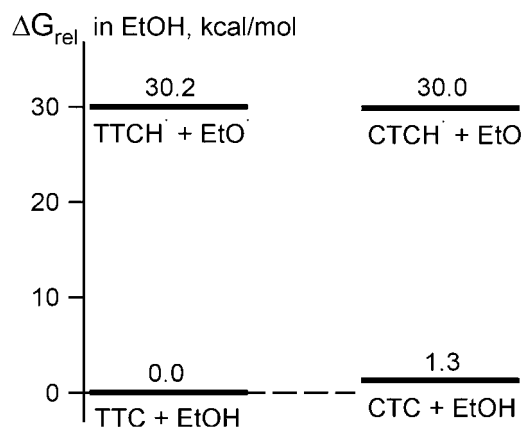
The *cis-trans* positions relative to three bonds linking the fragments of the spirocompound molecule make probable the existence of eight isomers of an open form.<sup>[13,55]</sup> Below, we will use the well-known designations<sup>[55]</sup> indicating position starting with the indoline part of the molecule. Among eight possible



**Scheme 3.** *Trans*-isomers of an open form of SNO



**Figure 10.** Relative Gibbs energies (in kcal mol<sup>-1</sup>) of the closed form A and *cis*- and *trans*-isomers of open form B of model SNO (Scheme 1, R = OH) predicted by the UPBE0/6-31G(d,p) method in ethanol at 298 K



**Figure 11.** Relative 298 K Gibbs energies (in kcal mol<sup>-1</sup>) of the formation of CTCH and TTCH radicals calculated by the PBE0/6-31G(d,p) method in ethanol. The sum of Gibbs energies of the CTC isomer and ethanol was set to zero

configurations, *cis*-isomers relative to the central bond (TCT, TCC, CCT, and CCC) are unstable due to the repulsion of two molecule fragments.<sup>[55]</sup> *Trans*-isomers, which are relatively stable, are shown in Scheme 3.

The primary photochemical process for spirooxazines is the break of the bond between the spiro carbon atom and the oxygen atom, which results in the formation of an

intermediate *cis-cisoid* isomers CCC and TCC.<sup>[56]</sup> The planes of indoline and oxazine moieties in *cis-cisoid* isomers are mutually perpendicular, which is similar to the geometry of a closed form. *Cis-cisoid* isomers bring up an association with Fisher's X-isomer<sup>[18,19]</sup>. Rotating the indoline and oxazine parts of the molecule relative to each other gives rise to the B-form isomers with a flat geometry (CTC and TTC).

Figure 10 shows the results of calculations for the model SNO molecule. TTC and CTC isomers have the lowest Gibbs energies among the isomers of an open form. They have flat geometry. Equilibrium between the two neighboring isomers determines the optical spectra of an open form of SNO.<sup>[37]</sup> TTT and CTT isomers, whose geometry is not completely planar, have sufficiently higher energies (Fig. 10). The energy gap between the closed form and CCC isomer corresponding to the barrier of the A → B reaction is ca. 14 kcal mol<sup>-1</sup>.

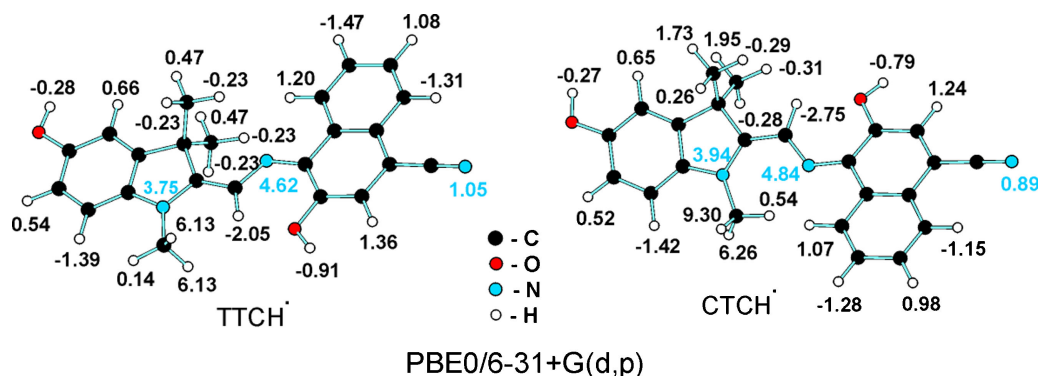
The calculated relative energies of *cisoid* and *transoid* isomers are in good agreement with previously reported calculations for similar molecules,<sup>[56–58]</sup> which supports the correctness of calculations performed in this work.

Calculations of structures and Gibbs energies of formation were performed also for the radicals obtained by addition of an H-atom to the naphthooxazine ring oxygen atom of the most stable merocyanine isomers TTC and CTC. Figure 11 demonstrates that reaction of the hydrogen abstraction from ethanol by TTC and CTC isomers is endothermic, and at least 30 kcal mol<sup>-1</sup> of energy is necessary for its passing.

Quantum chemical calculations of the UV spectra of the merocyanine radicals were performed to assign the experimental spectra. According to TD-UPBE0/6-31+G(d,p) calculations, the TTC (CTC) radicals have a very intense absorption band in the region of 544 (551) nm and a less intense band in the region of 688 (700) nm in ethanol. The calculated positions and oscillator strengths of the absorption bands (which are shown as vertical bars in Fig. 5) are in a fine agreement with the UV spectrum of the C-form of SNO3.

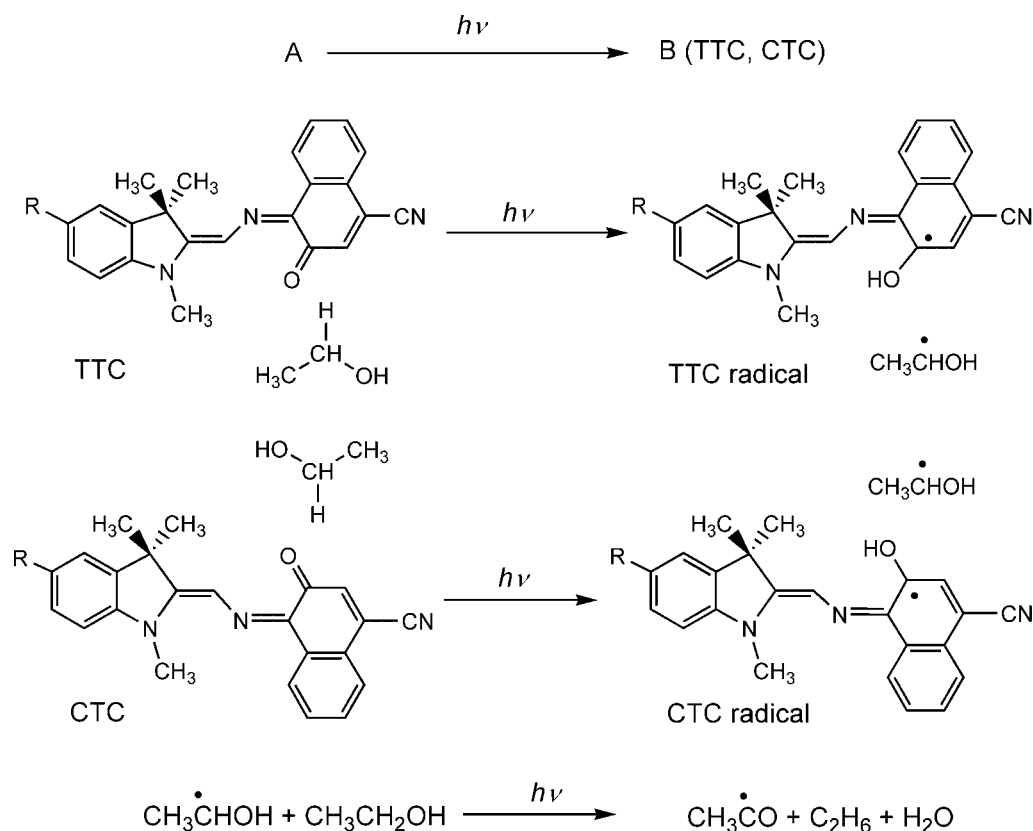
Calculated by the UPBE0/6-31G(d,p), hyperfine constants (Fig. 12) were used to model the ESR spectra of the merocyanine radicals. Taking the linewidth of individual components of hyperfine structure  $\Delta H = 5$  G (which is typical for free radicals in frozen matrices), we obtain that the ESR spectrum of the merocyanine radical is a singlet line at  $g \approx 2$  with a linewidth of ca. 15 G. This is in a good coincidence with the experiment.

Therefore, the results of quantum chemical calculations support the experimental data. It should be stressed that the



**Figure 12.** Calculated by the UPBE0/6-31G(d,p) hyperfine constants on hydrogen and nitrogen atoms of the merocyanine radicals. Nitrogen atoms are marked as gray circles





**Scheme 4.** Formation of radicals in a course of SNO photolysis in ethanol matrix

two types of free radicals are formed having similar ESR spectra, namely a merocyanine radical (C-form) and acyl radicals (which could be both  $\text{CH}_3\dot{\text{C}}\text{O}$  and  $\text{CH}_3\text{CH}(\dot{\text{C}}\text{O})\text{OH}$ ).

## CONCLUSIONS

The experiments with SNO did not give evidence of the stabilization of *cis-cisoid* isomers (which could be considered as Fisher's X-isomer<sup>[18,19]</sup>) in a low temperature matrix. Instead, the photolysis of the B-form of SNO3 was shown to result in the formation of a new species (C-form) having both UV and ESR spectra. The C-form was identified as a radical of the merocyanine resulted by abstraction of an H atom from the solvent molecule to the light-excited B-form. The schematic mechanism of the reaction for the most stable merocyanine isomers TTC and CTC is shown in Scheme 4 (the transformations of acyl radicals are not shown for simplicity). The formation of a merocyanine radical represents a new specific channel of photochemically induced degradation of spirooxazines which takes place in frozen alcohol matrices. The same process is to be expected for spirooxazines incorporated to the hydrogen-containing polymeric matrices.

Among three studied SNO, the formation of merocyanine radicals was observed only for SNO3 having the longest substituent in the indoline moiety of the molecule (Scheme 2). The mechanism of the effect of the aliphatic substituent length in the indoline moiety on the ability of the oxygen atom in the oxazine moiety to add a hydrogen atom is not clear.

Probably, the difference is determined by the lowest value of the quantum yield of  $\text{B} \rightarrow \text{A}$  reaction in the case of SNO3

photolysis at 365 nm. One can imagine that the existence of the long substituent exactly in the case of SNO3 hindered the mutual rotation of indoline and oxazine moieties which is necessary for the formation of a closed form. As a result, an alternative reaction with a lower quantum yield ( $\text{B} + \text{EtOH} \rightarrow \text{Radicals}$ ) becomes observable.

Another possibility is that the primary event of the H atom abstraction from the solvent molecule could be the formation of a very short-lived intramolecular biradical resulted by the photoinduced hydrogen atom transition from the 5-O-n-alkyl substituent to the oxazine moiety. This biradical could be further stabilized by the H atom transfer from the solvent to the C16 chain. C3 and C9 chains would be too short to allow this intramolecular biradical formation, which explains the occurrence of the radical only in the case of SNO3. For sure, both explanations are tentative and should be supported by the quantum chemical calculations performed on the real compounds.

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