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Peculiarities of photochromic behaviour of spiropyrans and spirooxazines

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Abstract

A comparative analysis of the spectral and photochromic properties of nitrosubstituted indolinic spirobenzopyrans (SBPs) and spironaphthooxazines (SNOs) is presented. Formation of the same trans isomer of the SNO coloured form at any temperature over a wide range (77–300 K) is proposed contrary to the case of SBP for which the photoproduct structure depends on temperature. Such photochromic parameters as the quantum yields of photocolouration and spirobond C–O dissociation, and the efficiency of photoinduced form stabilization are examined for nitrosubstituted SBPs and SNOs. © 1997 Elsevier Science S.A.

Keywords: Luminescence; Photochromism; Spironaphthooxazine; Spiropyran

1. Introduction

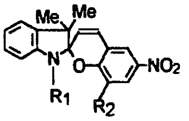
Photochromism discovered as far back as the last century now attracts much attention because of the potential for practical applications of photochromic systems as optical filters, optical switches, optical memory for computers, etc. Photochromism of organic compounds is the photoinduced transformation of a molecular structure, photochemically or thermally reversible, which produces a spectral change, typically, but not necessarily, of visible colour.

Spirocompounds are of particular concern among photochromic systems. Their photochromic transformation mechanism involves spirobond photodissociation and cis–trans isomerization to give highly coloured plane merocyanines. Spirobenzopyrans (SBPs) [1,2] are probably the most well-known class of organic photochromes. Spirooxazines and in particular spironaphthooxazines (SNOs) have been the subject of many investigations, owing to their higher photostability [3,4] in comparison with SBPs. At the same time, to our knowledge, no attempt has been made to compare and explain the basic distinction between SBP and SNO photochromic properties. Hence, in this paper we present a first attempt at a comparative analysis of the experimental data for nitrosubstituted SBPs and SNOs, and our hypothesis explaining SNO photochromic features.

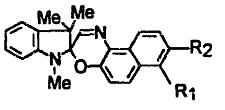
2. Experimental details

2.1. Materials

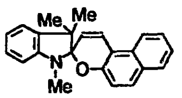
The objects under study were photochromic molecules having the following structure:



SBP	R_1	R_2
1	CH_3	H
2	$C_{16}H_{33}$	H
3	C_6H_5	H
4	CH_3	OCH_3



SNO	R_1	R_2
1	H	H
2	NO_2	H
3	H	NO_2



SNP

SBPs 1–4, SNOs 1–3 and SNP were prepared and purified as described in Refs. [5], [6] and [7]. Nuclear magnetic resonance and thin layer chromatography techniques showed no trace of impurities in these samples.

Glass-forming low temperature petroleum ether (PE) purified by a standard method was used as a solvent. Absorption spectra were measured in polymeric films.

The concentrations of the compounds were varied in the range 10^{-5}–10^{-6} mol dm^{-3}.

2.2. Luminescence quantum yield determination at 77 K

Phosphorescence quantum yields φ_{ph} were obtained by a relative method [8] using the following equation:

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$$\varphi=\varphi_r\left(\frac{n}{n_r}\right)\frac{D}{D_r}\frac{\int[R(\lambda)/S(\lambda)]\mathrm{d}\lambda}{\int[R_r(\lambda)/S(\lambda)]\mathrm{d}\lambda} \tag{1}$$

where the subscript "r" refers to the reference sample, n is the refractive index of the solvent, $S(\lambda)$ is the spectral quantum sensitivity of the measuring system, $R(\lambda)$ is a luminescence spectrum, and D is the optical density of the sample at the excitation wavelength.

The determination of luminescence quantum yields is a simple procedure at room temperature, becoming rather complicated at the liquid nitrogen temperature owing to the absence of suitable standard samples with correctly measured quantum yields at 77 K. Therefore, two correction factors need to be taken into account using standard sample data at room temperature. The first correction is necessary to compensate for the different solvent refractive indexes at room temperature and 77 K. The second one takes into account the refractive index of liquid nitrogen surrounding the cell. It is known [9] that the refractive index n and density d are related by the following empirical equation:

$$\frac{n^2-1}{n+0.4}\frac{1}{d}=C \tag{2}$$

where C is a constant depending on the solvent used.

Thus, we can define the refractive index at 77 K n_{77} using n at 300 K (n_{300}) and the change in d on the transition from 300 to 77 K. n_{300} for PE is equal to 1.38. The change in d for any solvent is equal to its volume change. For solvent contraction determination, a certain volume V_{300} was placed in a cylindrical cell and the meniscus position was registered, the cell then being placed in a glass Dewar flask containing liquid nitrogen. A sharp image of the cell with glassed solvent was projected onto a screen and the solvent volume at 77 K V_{77} was calculated. For PE it was found that

$$V_{300}/V_{77}=d_{77}/d_{300}=1.43$$

and then n_{77} was calculated by Eq. (2) ($n_{77}=1.56$).

The second correction factor taking into account the influence of liquid nitrogen on the luminescence signal was obtained by the following method. A solution of SBP-4 in PE was placed in the Dewar flask containing liquid nitrogen, and 365 nm wavelength light was used to excite SBP phosphorescence, the intensity of which did not change during irradiation because SBP-4 was discovered to be nonphotochromic under these conditions. After recording the phosphorescence signal, the liquid nitrogen was quickly evaporated and the phosphorescence measured again. The second signal was more intensive; a correction factor of 1.3 was obtained which did not change in the wavelength region 450–600 nm.

Solutions of quinine bisulphate in 1 N H_2SO_4 and fluoresceine in carbonate–bicarbonate buffer were used as standards in the luminescence quantum yield determination [8].

2.3. Definition of quantum yield of photocolouration

Photocolouration of spirocompounds was carried out in PE at 77 K. The phosphorescence intensity of the initial form A was measured on the equipment described in Ref. [10] during UV irradiation, giving the kinetics of photocolouration. The intensity of excited light at 365 nm was approximately 3×10^{-8} Einstein cm^{-2} s^{-1}.

The optical scheme of luminescence registration shown in Fig. 1 ensured homogeneity of the excitation beam and proportionality of the luminescence intensity with substance concentration. All spectral measurements were carried out in a quartz rectangular cell (**1**). The excitation light beam (**2**) had a rectangular section 2×5 mm^2 on the front face of the cell. The analysing monochromator detected light radiated by the sample volume with a cross dimension m/G, where m is the width of the entrance slit, and G is the magnification of the system and is equal to S_2/S_1 (see Fig. 1). When $m=0.5$ mm, $G=3$ and $D=1$ (D is the 1 cm length optical density of the solution), the optical density of the detected region of the sample did not exceed 0.02. This meant that the excitation light intensity was nearly constant in the limits of the cross section of this region. The operative height of the entrance slit was 1 mm.

The concentration of the spirocompound initial form A at a distance l from the front cell surface during photocolouration by the light intensity I_0 at the excitation into the isosbestic point with coefficient of extinction ε is described by the following equation [11]:

$$A(t,l)=A_0\exp[t\varepsilon\varphi_{AB}I_0\exp(-\varepsilon A_0 l)] \tag{3}$$

This means that a substance layer of thickness l is a constant optical density filter for excitation light. Therefore, φ_{AB} can be determined using Eq. (3). The isosbestic point was obtained by measuring the absorption spectrum at different degrees of transformation of the initial form to the photoinduced form for every compound. φ_{AB} was then calculated using

$$\varphi_{AB}=-\frac{1}{\varepsilon I_0 e^{-\varepsilon A_0 l}}\frac{\mathrm{d}(\ln I_{ph})}{\mathrm{d}t} \tag{4}$$

where I_{ph} is the intensity of measured phosphorescence.

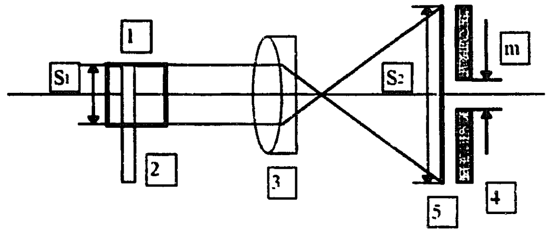


Fig. 1. Optical scheme of luminescence measurement in the study of phototransformation kinetics in rigid matrixes: 1, sample; 2, photoactivating light beam; 3, short-focus condenser; 4, analysing monochromator slit; 5, image of a sample section exposed to photolysis in the slit plane.

Table 1
Photophysical parameters of the initial form molecules of nitrosubstituted SBP and SNO at 77 K in PE

Compound	φ_{ph}	φ_{AX}	τ_{ph}, s	φ_{br}	φ_{st}
SBP-1	0.005	0.06	0.035	0.86	0.07
SBP-2	0.007	0.02	0.035	0.80	0.025
SBP-3	0.012	0.009	0.024	0.50	0.02
SBP-4	0.25	0	0.23	0.5	0
SNO-1	0	–	–	1	–
SNO-2	0.007	0.002	0.014	0.51	0.0039
SNO-3	0.002	0.004	0.015	0.89	0.0045

3. Results and discussion

3.1. Kinetics of photocolouration at 77 K

It was proposed in Ref. [12] and later experimentally proved by the polarized luminescence method [13,14] that the cis–cisoid isomer X, having a structure similar to that of the initial form A but with a dissociated C–O spirobond, is the main product of SBP photocolouration in a nonpolar matrix at 77 K.

The study of the photocolouration kinetics of nitrosubstituted SBPs and SNOs showing phosphorescence in PE at 77 K led to the following results.

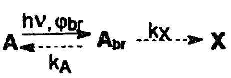
(1) The spectrum, quantum yield φ_{ph} and lifetime τ_{ph} of form A phosphorescence (Table 1) are time independent during the photocolouration process.

(2) Photocolouration kinetics is nonexponential owing to the heterogeneity of the solid matrix.

(3) The photocolouration quantum yield φ_{AX} calculated by Eq. (4) is independent of the light intensity but permanently decreases during irradiation (e.g. for SBP-1 $\varphi_{AX}=0.06$ initially and 0.001 after 150 s irradiation). Initial values of φ_{AX} for the studied spirocompounds are given in Table 1.

(4) No photobleaching process of isomer X is observed in PE matrix at 77 K.

From these data and the fact that the photocolouration quantum yield at 77 K (φ_{AX}) is smaller than that at 300 K (φ_{AB}) (for SBP-1 $\varphi_{AB}=0.6$ [2]), we conclude that φ_{AX} is not a fundamental characteristic of the intramolecular process of electronically excited state deactivation for the initial form A molecule. In other words, if such a characteristic as the quantum yield of spirobond C–O breakage φ_{br} is introduced, it could be proposed that $\varphi_{AX}\equiv\varphi_{br}$, but this is not the case. Consequently, in order to explain the φ_{AX} dependence on irradiation time (while φ_{ph} and τ_{ph} are time independent), we assume a modification of the scheme of the photocolouration process as shown below:



$$A \underset{k_A}{\overset{h\nu,\varphi_{br}}{\rightleftarrows}} A_{br} \xrightarrow{k_X} X \qquad (5)$$

where A_{br} is a spirocompound molecule with a broken spirobond, and k_A and k_X are the rate constants of dark reactions depending on the temperature and viscosity of the medium. This means that the experimentally measured quantum yield of X isomer formation is related to φ_{br} by the equation

$$\varphi_{AX}=\varphi_{br}\frac{k_X}{k_X+k_A} \qquad (6)$$

We can conclude that φ_{br} like φ_{ph} and τ_{ph} is defined by intramolecular radiative and nonradiative deactivation of the excited states of the molecule and does not depend on the colouration time. Consequently, the dispersion of φ_{AX} is caused by the dispersion of the dark reaction rate constants. This approach explains the relationship $\varphi_{AX}<\varphi_{AB}$ because the k_X value at 300 K may be significantly greater than that at 77 K. If the proposed Eq. (5) is true a question arises about the X isomer structure. We can make two suggestions concerning its nature. Firstly, the X isomer is identical to the A_{br} molecule, but the former is stabilized owing to a rearrangement of the solvent molecules. This rearrangement is likely to be possible because of the following fact. The energy of spirobond C–O breakage (E_{br}) usually lies in the region 21–57 kcal mol^{-1}, depending on the structure of the spirocompound. An excess of absorbed energy ($h\nu - E_{br}=26$–62 kcal mol^{-1}) then relaxes into the surroundings of the photochromic molecule, causing local warming of the glassy matrix and therefore increasing the lability of the neighbouring solvent molecules. Secondly, X isomer stabilization may occur by virtue of a small rotation of two orthogonal parts of the molecule due to above-mentioned local matrix warming. It seems most likely that the simultaneous action of both these factors is necessary for X isomer stabilization.

3.2. Quantum yield of spirobond breakage

As shown above, the direct experimental measurement of the quantum yield of spirobond breakage at 77 K is not possible, and so φ_{br} determination requires calculation from other experimentally measured fundamental parameters. This calculation, in turn, requires a knowledge of the relation between these parameters which is defined by the photophysical mechanism of the photochromic process. A literature survey does not result in clear conclusions about the relative contributions of singlet and triplet excited states to the photochromic transformation of spirocompounds and the influence of molecule structure on them. Therefore, a common case of radiative and nonradiative transitions in the form A molecule after excitation into the first singlet state S_1 will be considered (Fig. 2).

The following symbols are used in Fig. 2 for rate constants of the elementary processes: k^s_{br} and k^i_{br} are the rate constants of the spirobond dissociation in the singlet state S_1 and triplet state T_1 from vibrational excited level i respectively; d and d_i are those of internal conversion in the system of the singlet and triplet levels respectively; q_1 and q_2 are those of intersystem crossing; p and f are those of phosphorescence and fluorescence emission respectively.

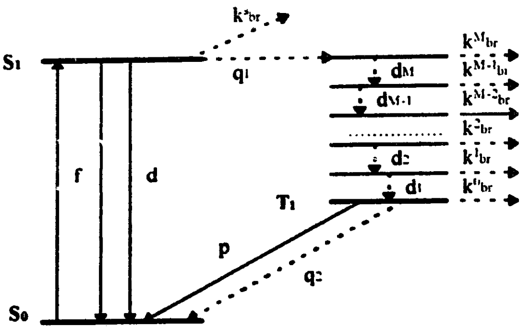


Fig. 2. Scheme of radiative and nonradiative transitions in the initial form molecule of a spirocompound.

Using the scheme in Fig. 2, the following equations can be written for the quantum yields of spirobond breakage in the systems of the singlet (φ_{br}^{s}) and triplet (φ_{br}^{t}) levels, and the quantum yields of phosphorescence state (φ_{t}) and fluorescence (φ_{f}):

$$\varphi_{br}^{s}=\frac{k_{br}^{s}}{k_{br}^{s}+q_{1}+d+f} \qquad (7)$$

$$\varphi_{br}^{t}=\frac{q_{1}}{k_{br}^{s}+q_{1}+d+f}\left[\frac{k_{br}^{M}}{k_{br}^{M}+d_{M}}+\sum_{i=1}^{M-1}\left(\frac{k_{br}^{i}}{k_{br}^{i}+d_{i}}\prod_{j=i+1}^{M}\frac{d_{j}}{k_{br}^{j}+d_{j}}\right)\right]+\varphi_{t}\frac{k_{br}^{0}}{k_{br}^{0}+p+q_{2}} \qquad (8)$$

$$\varphi_{t}=\frac{q_{1}}{k_{br}^{S}+q_{1}+d+f}\prod_{i=1}^{M}\frac{d_{i}}{k_{br}^{i}+d_{1}} \qquad (9)$$

$$\varphi_{f}=\frac{f}{k_{br}^{s}+q_{1}+d+f} \qquad (10)$$

Eq. (8) is a sum of the probabilities φ_{br}^{i} of spirobond breakage for each vibronic level i of the triplet state. In fact, the probability for the upper level M is

$$\varphi_{br}^{M}=\frac{q_{1}}{k_{br}^{s}+q_{1}+d+f}\frac{k_{br}^{M}}{k_{br}^{M}+d_{M}}$$

The same probability for the following level $M-1$ is

$$\varphi_{br}^{M-1}=\frac{q_{1}}{k_{br}^{s}+q_{1}+d+f}\frac{d_{M}}{k_{br}^{M}+d_{M}}\frac{k_{br}^{M-1}}{k_{br}^{M-1}+d_{M-1}}\text{ etc.}$$

Summing up all the probabilities from M to 0 gives Eq. (8).

$\varphi_{br}=\varphi_{br}^{s}+\varphi_{br}^{t}$ can then be expressed by mathematical transformations of Eqs. (7)–(10) as

$$\varphi_{br}=1-\frac{d}{k_{br}^{s}+q_{1}+d+f}+\varphi_{t}\frac{k_{br}^{0}}{k_{br}^{0}+p+q_{2}}-\varphi_{t}-\varphi_{f} \qquad (11)$$

The maximum value of k_{br}^{0} may be estimated from

$$\tau_{ph}=\frac{1}{k_{br}^{0}+p+q_{2}} \qquad (12)$$

assuming $p=q_{2}=0$, i.e. $(k_{br}^{0})_{max}=1/\tau_{ph}$. The result for SBP-1 obtained in this manner (≈ 28 s^{-1}) is some orders of magnitude smaller than the spirobond breakage rate constant ($>10^{11}$ s^{-1}) measured in Ref. [15] by pulse photolysis. From these data, we conclude that the zero vibration level of the triplet state takes no part in the photochromic process. This conclusion is consistent with the results of Ref. [16], in which the sensitivity of SBP photocolouration to triplet energy donors was studied and it was shown that the photoactive triplet level of the initial form **A** molecule lies above the phosphorescence level.

Taking into account that the probability of internal conversion $S_1 \rightarrow S_0$ for most organic compounds in rigid matrixes at 77 K is small [17], i.e. $d=0$, and that no fluorescence is observed for all the spirocompounds studied, Eq. (11) may be simplified as

$$\varphi_{br}=1-\varphi_{t} \qquad (13)$$

Using $\varphi_{ph}=\varphi_{t}\cdot p\cdot\tau_{ph}$ gives

$$\varphi_{br}=1-\frac{\varphi_{ph}}{p\tau_{ph}} \qquad (14)$$

Thus, the desired φ_{br} may be derived from the experimentally measured parameters φ_{ph} and τ_{ph} using Eq. (14). However, knowledge of the rate constant of phosphorescence emission is necessary too. It is known that the benzopyran and naphthooxazine fragments are the emission centres in nitrosubstituted SBPs [2] and SNOs [18] respectively. According to Ref. [17], $p\sim 1$ s^{-1} for nitrobenzene, 1-nitronaphthaline and 1,5-dinitronaphthaline, and so this estimation value was used in the present work for all the compounds studied except SBP-4 and SNO-1. For SBP-4, we used $\varphi_{t}=0.5$ [19]. The closed form molecule of unsubstituted SNO-1 shows neither fluorescence nor phosphorescence in PE at 77 K and so $\varphi_{ph}=\varphi_{f}=0$, i.e. $\varphi_{br}=1$. Thus, the φ_{br} values listed in Table 1 were obtained for all spirocompounds discussed. Then using the following equation

$$\varphi_{st}=\varphi_{AX}/\varphi_{br} \qquad (15)$$

the efficiencies of **X** isomer stabilization in PE at 77 K were calculated. Table 1 data examination indicates an important feature: for all the SNOs studied the φ_{AX} and φ_{st} values are an order of magnitude smaller than those for the SBPs. The sense of this basic distinction will be discussed below.

3.3. Absorption spectra of the photoinduced form

It is well known [2] that the absorption spectra of the SBP coloured form **B** depend on the irradiation temperature. This dependence is connected with the existence of different stereoisomers of the **B** form. These stereoisomers have individual spectral characteristics, and exist in thermodynamic equilibrium depending on the temperature and medium properties. Using the polarized luminescence method in our previous papers [13,20,21], we have managed to determine a correspondence between spectral characteristics and stereoisomer structure, and to follow the sequence of isomer transformations for the SBP photoinduced form with increasing temperature from the cis–cisoid **X** isomer at 77 K to the most stable trans isomer of **B** at 300 K. In addition, it has been

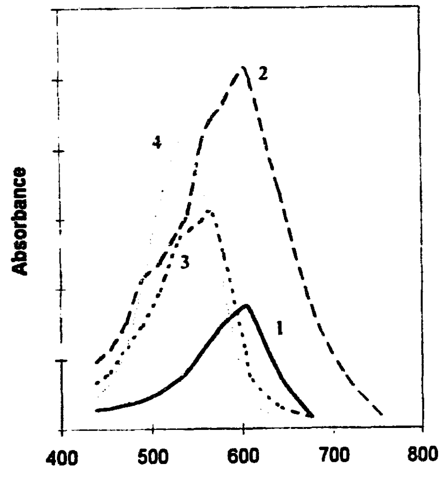


Fig. 3. Absorption spectra of the photoinduced form of SNO-1 in polyvinylbutyralic film (1,2) and that of SNP in poly(methyl)metacrylatic film (3,4) at 283 K (1), 196 K (3) and 77 K (2,4).

found that in polar solvents several stereoisomers of the coloured form may exist at the same temperature.

Contrary to SBPs, the absorption spectra of SNO photoinduced forms are temperature independent, both in solvents of different polarities [3,10] and in polymer matrixes [22] over a wide temperature range 77–300 K. The absorption spectra of the coloured forms of SNO-1 and its pyram analogue SNP at two different temperatures are shown in Fig. 3. The coincidence of two SNO-1 spectra is evident while two SNP spectra clearly differ in longwave maximum position. The absorption spectra of nitrosustituted SNO studied in the present work are temperature independent too. It is found in Ref. [10] that the temperature dependence of the absorption spectra of the photoinduced forms for SNOs having electron-donor substituents (piperidine or morpholine) in nonpolar heptane and PE is caused by molecular aggregation and vanishes at low concentrations. Thus, it is reasonable to suppose that temperature independence of SNO coloured form absorption spectra is a common property for all photochromic spirooxazine compounds.

3.4. *Peculiarities of SNO photochromism*

The temperature independence of the absorption spectra of the SNO coloured form allows the assumption that the colouration process of any SNO at any temperature (in the region 77–300 K), contrary to SBP, leads to the formation of the same photoinduced stereoisomer. This photoproduct cannot have cis–cisoid structure because in this case its rate constants of dark decolouration at room temperature must be some orders of magnitude larger than the experimentally measured ones, owing to the absence of a trans–cis isomerization stage in the decolouration process. Moreover, in this case the activation energy of decolouration must be ≈ 20 kcal mol^{-1} independent of matrix rigidity as this value is typical for SBPs and SNOs in liquid solutions [2], i.e. under such conditions when only the ring closure is the limiting stage of the decolouration process. The same value was obtained for SNO-1 solution in EtOH [3]. If it is supposed that the cis–cisoid **X** isomer of SNO is formed both in rigid polymer matrixes and in solutions, then the activation energy of decolouration in polymers should be approximately the same as in liquid solution. However, as shown in Ref. [22] the activation energy of decolouration of the SNO-1 **B** form in polymer matrixes lies in the range 4–10 kcal mol^{-1}, depending on the polymer nature, and for nitrosubstituted SNO-2 and SNO-3 it is equal to 2–6 kcal mol^{-1} [23].

Hence, it is reasonable to assume that photocolouration of SNOs even at low temperatures includes cis–trans isomerization leading to the formation of the coloured trans isomer (with the exception of SNOs [24] in which indoline and naphthooxazine fragments are chemically connected by a bridge between positions 3′ and 2, preventing rotation of constitutive parts of the molecule). Consequently, Eq. (5) representing the process of SBP photocolouration at 77 K may be corrected for SNOs by including the stage of trans isomer **B** formation:

$$\mathrm{A}\underset{k_A}{\overset{\varphi_{br}}{\rightleftarrows}}\mathrm{A_{br}}\underset{k_{Abr}}{\overset{k_X}{\rightleftarrows}}\mathrm{X}\xrightarrow{k_B}\mathrm{B} \qquad (16)$$

If this assumption is true, then the quantum yield of SNO photocolouration is given by

$$\varphi_{AB}=\varphi_{br}\frac{k_Bk_X}{k_Bk_X+k_Ak_{Abr}+k_Ak_B} \qquad (17)$$

Thus, just the assumption that SNO photocolouration leads to trans isomer formation even at 77 K explains the low values of both the quantum yield of photoinduced product formation and the efficiency of its stabilization at 77 K in comparison with that for SBP. In other words, the SNO photocolouration (Eq. (16)) differs from Eq. (5) applied to SBP photocolouration by an additional reversible stage, and so the φ_{AX} data for SNOs given in Table 1 should really be referred to as φ_{AB}.

The process of formation of the coloured trans isomer of the spirocompounds necessarily includes rotation about the double bond C=C for SBPs or C=N for SNOs. In the latter case, this process is essentially facilitated because it is known [25,26] that the energy barriers to -N= atom inversion or that of rotation about the C=N bond equal to 18–20 kcal mol^{-1} are smaller than the energy barrier to rotation about the C=C bond (40–65 kcal mol^{-1}). Besides, so long as the side irreversible reactions causing the loss of photochromic properties take place mainly after spirobond dissociation [2], these reactions and cis–trans isomerization of the **X** isomer into the trans isomer **B** are competitive processes, and it is likely that just the ease of SNO isomerization is responsible for the improved photostability of SNO in comparison with SBP molecules.

4. Conclusions

The data obtained in the present work allow us to suggest that the difference between the photochromic properties of SNOs and SBPs is likely to be connected with a greater tendency of the former for cis–trans isomerization.

Moreover, analysis of the data shown in Table 1 leads us to two more conclusions. Firstly, the photochromic behaviour of spirocompounds (such as SBPs or SNOs) is determined not by the quantum yield of spirobond breakage φ_{br}, which is rather high for all the compounds studied, but by the efficiency of stabilization of the photoinduced form φ_{st}, depending on molecular structure and external conditions. As an example, φ_{st} for SBP-4 is equal to 0 at 77 K in PE, but at 300 K this SBP exhibits strong photochromic properties. Secondly, more effective population of the zero vibration level of the initial form A triplet state leads to a decrease in both φ_{br} and the photostability. So, it was shown [18,23] that the photostability of nitrosubstituted SNOs is less than that of SNO-1, and SNO-3 is the most stable among the nitrosubstituted SNOs.

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