

Photo- and thermochromism. II.

Effect of conjugation on the absorption intensity of nitro group of 8-bromo-1',3',3'-trimethyl-6-nitrospiro(chromene-2,2'-indoline)

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The paper deals with the reversible changes of absorption intensities of the nitro group of 8-bromo-1',3',3'-trimethyl-6-nitrospiro(chromene-2,2'-indoline) doped into a polyacrylonitrile thin film in the infrared region. The X-ray structural analysis proved the random orientation of pyrans in the polymer matrix. The reversible changes of absorption intensities of the symmetrical and asymmetrical nitro group vibrations were explained by the altered conjugation of pyrans upon exposure to irradiation.

The photochromic properties of 8-bromo-1',3',3'-trimethyl-6-nitrospiro(chromene-2,2'-indoline) (SP) doped into a polyacrylonitrile (PAN) thin film were studied in Part I of this work [1] from the changes of spectra in the infrared region. The hypothesis of uniform orientation of SP in PAN was forwarded on the basis of the reversible changes of absorption intensities of the nitro group.

In this paper the possibility of preferable orientation of SP in PAN was tested by the X-ray structural analysis. The reversible changes of absorption intensities of the nitro group were explained by altered conjugation during photochromic transformations of SP.

Experimental

The samples were prepared by the same method as in [1]. The spectra in the infrared region (Fig. 1) were recorded on a Perkin-Elmer 125 spectrophotometer equipped with a Golay detector.

The orientation degree of SP in PAN was studied by the Debye-Scherrer method. Diffractions were recorded in the range of angles $2\theta = 10-50^\circ$ on a Philips apparatus. The diffraction spectra are in Fig. 2.

Discussion

According to the results obtained with the spiro compounds of pyrans having different substituents, the "photosensitive" absorption bands at 1340 and 1515 cm^{-1} (Fig. 1) correspond to the symmetrical and asymmetrical nitro group vibrations. In the course of SP phototransformation the intensities of the nitro group stretching vibration bands changed in the reverse direction; formation of the coloured form was characterized by a decrease in the intensity of symmetrical vibration whereas the intensity of asymmetrical

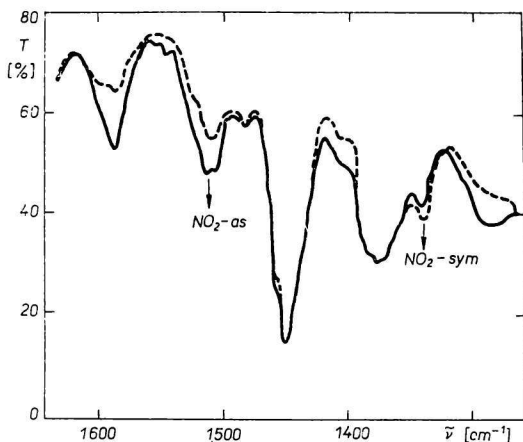


Fig. 1. Change of the absorption intensity of symmetrical (1340 cm^{-1}) and asymmetrical (1515 cm^{-1}) nitro group vibrations in the course of SP photochromic transformations. ——— photocoloration of SP; - - - photobleaching of SP.

vibration increased. In colourless form it was *vice versa*. To explain this phenomenon the hypothesis of the uniform orientation of SP in PAN was suggested. The orientation of SP in coloured form was expected to be perpendicular to the thin film plane and parallel to the radiation propagation. In such an arrangement, only the vector of dipole moment corresponding to the asymmetrical vibration could interact with the \vec{E} vector of radiation. We assumed that the colourless form was arranged in such a way that the part of SP molecule containing nitro group was located in the plane of the PAN matrix. The orientation degree of SP in various media could be determined from the difference of photobleaching efficiency supposing that the efficiency is independent of the

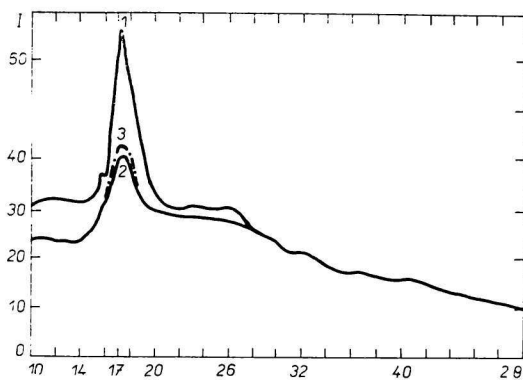


Fig. 2. Dependence of the diffraction intensity on the diffraction angle for: 1. PAN matrix; 2. PAN matrix + SP (photocoloration); 3. PAN matrix + SP (photobleaching).

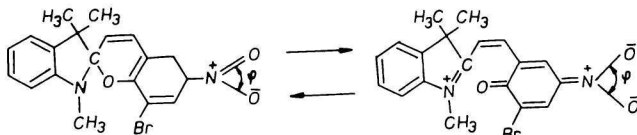
interaction of SP with its matrix. This assumption could be approached when studying photobleaching in the liquid phase. In the solid state SP forms aggregates from dimers to multimers the quantum yields of which are substantially lower than those of monomers. Moreover, they differ one from the other. Therefore the orientation degree of SP in PAN was studied by the X-ray analysis. Fig. 2 shows the dependence of the diffraction intensity upon the incidence angle of X-ray radiation for different samples. For the PAN matrix the maximum of the diffraction intensity was observed at $2\theta = 17^\circ$ corresponding to the lattice parameter 5.2 Å and being in good agreement with the literature [2]. This diffraction can be interpreted as the (100) diffraction of a hexagonal lattice.

With regard to a considerable amount of the solvent—dimethylformamide (20% transmittance at 1670 cm^{-1}), a random orientation of SP in PAN might be expected. However, it was not clear what role played SP in the formation of the PAN thin film structure. In case SP is a nucleation centre in PAN, its addition into PAN will result either in an increase of the diffraction maximum intensity at $2\theta = 17^\circ$ or other PAN structures will arise showing new diffraction maxima. It is evident from Fig. 2 that addition of SP caused none of these phenomena; moreover, the orientation degree of PAN decreased. In the course of photobleaching a small increase in the diffraction maximum intensity was recorded; however, its value did not reach that of the maximum of the pure PAN matrix.

It is probable that the reversible changes of absorption intensities of the nitro group vibrations were affected during SP phototransformations by changes of the π -electron distribution as a result of interaction with radiation ($\lambda \leq 360\text{ nm}$) or by dissolving SP in a matrix having a high value of permittivity. During phototransformation the SP molecule became conjugated and the changed electron distribution affected the dipole moment of individual parts of SP and consequently the absorption intensities in the infrared region [3]. According to [4], the absorption intensities of asymmetrical and symmetrical vibrations are related by:

$$\frac{\Gamma_{as}}{\Gamma_s} = \frac{\sin^2 \varphi/2}{\cos^2 \varphi/2},$$

where φ is the angle among the O—N—O atoms. Experimental verification of this explanation would prove the interpretation of reversible changes of the nitro group stretching vibrations (Scheme 1). A number of authors discussed the problem of the



Scheme 1

change of absorption intensities of the XY_2 group stretching vibrations; e.g. Zahradník *et al.* [5] presented a quantum-chemical interpretation of this effect together with experimental material. Therefore we expect our explanation to be sufficiently supported by this material.

References

1. Leščinský, M., *Chem. Zvesti* **23**, 194 (1969).
2. Bohn, C. R., Schaeffgen, J. R., and Statton, W. O., *J. Polym. Sci.* **55**, 531 (1961).
3. Davies, M., *Infrared Spectroscopy and Molecular Structure*, p. 340. Elsevier, Amsterdam, 1963.
4. Steele, D., *Quart. Rev.* **18**, 21 (1964).
5. Zahradník, R. and Boček, K., *Collect. Czech. Chem. Commun.* **26**, 1733 (1961).

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