

Photo- and Thermochemistry. I. Infra-red Spectra of 1,3,3-Trimethylindoline-6'-nitro-8'- -bromobenzopyrylospirane Doped in Polyacrylonitril Thin Film

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The photo- and thermochemistry of 1,3,3-trimethylindoline-6'-nitro-8'-bromobenzopyrylospirane doped in polyacrylonitril thin film was studied on the basis of changes of the infra-red spectra of complex solid solution. From reversible changes of „sensitive“ absorption bands in connection with chemical changes in the course of spirane-merocyanine transformations, their probable assignment was made. From the changes of $-\text{NO}_2$ group vibrations, stereo rearrangement is expected.

The spiropyranes are very promising compounds for solving a number of problems of applied science; *e.g.* they can be used as memory elements in computers. The photochromic effect — a sharp reversible change in the absorption spectra as the result of interaction with a light quantum — is produced in this class of compound because the spirane noncoplanar configuration which absorbs in the near ultra-violet region, is transformed into a merocyanine form as a result of breaking of C—O bond and of spatial rearrangement. This rearrangement results in coplanarity of the two parts of the molecule with pooling of the originally independent π electrons; a strong absorption band is observed in the visible region, ϵ is the order of 10^4 .

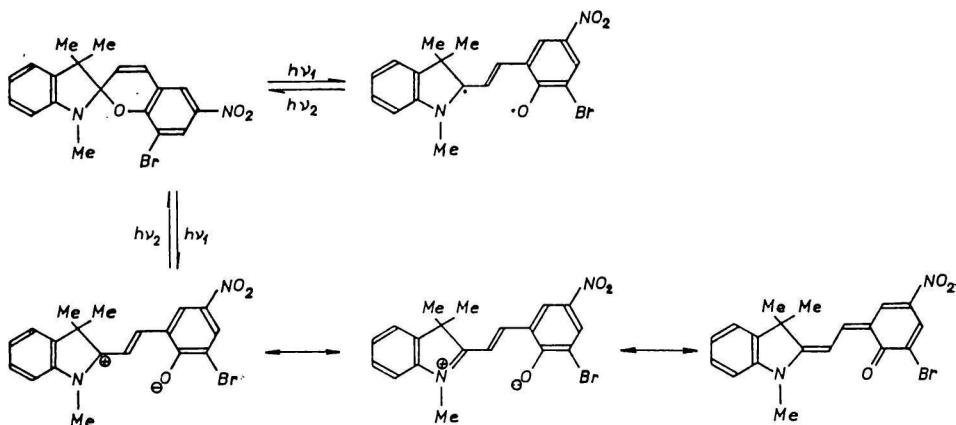


Chart 1

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Rotations of the two parts of the ionized merocyanine molecule is hindered because of the spatial and electrostatic circumstances and coloured states appear in a number of stereoisomeric forms which make the investigation of photoprocess and interpretation of the photochemical mechanism in spiropyranes difficult.

We made an attempt to follow the photochemical transformations in 1,3,3-trimethylindoline-6'-nitro-8'-bromobenzopyrylospirane (hereafter SP) (Chart 1) on the basis of changes in infra-red spectra. The behaviour of certain absorption bands is used to study the thermo- and photochromism of SP in solid solution of polyacrylonitril (hereafter PAN). No attempt has been made to obtain quantitative results.

Experimental

One gram of PAN ($\bar{M} = 75\ 000$) was dissolved in 100 g of dimethylformamide and a known amount of SP was doped. The viscous solution was subsequently evaporated on polished surface at temperature of about 70°C, the duration of evaporation varied from several hours to several days. Under the conditions of experiment, the thermal spirane \rightleftharpoons merocyanine equilibrium was shifted markedly toward the coloured merocyanic form [1].

For irradiation we employed the SH 100 high-pressure mercury arc. A major fraction of the UV light from this lamp occurred at wavelengths longer than 2800 Å, though two broad weak bands, 2540 and 1850 Å, were also emitted. To measure the dependency of the colour formation on the wavelength, several kinds of glass filter were applied.

Infra-red spectra were obtained with Hitachi spectrophotometer, Model EPI-510, at room temperature. All probable orientation of *E*-vector occurred in the plane of thin film.

The reagents were supplied by Dr. *T. Fukutomi* and Mr. *Kikuchi* from Polymer Department, Tokyo Institute of Technology and used without further purification.

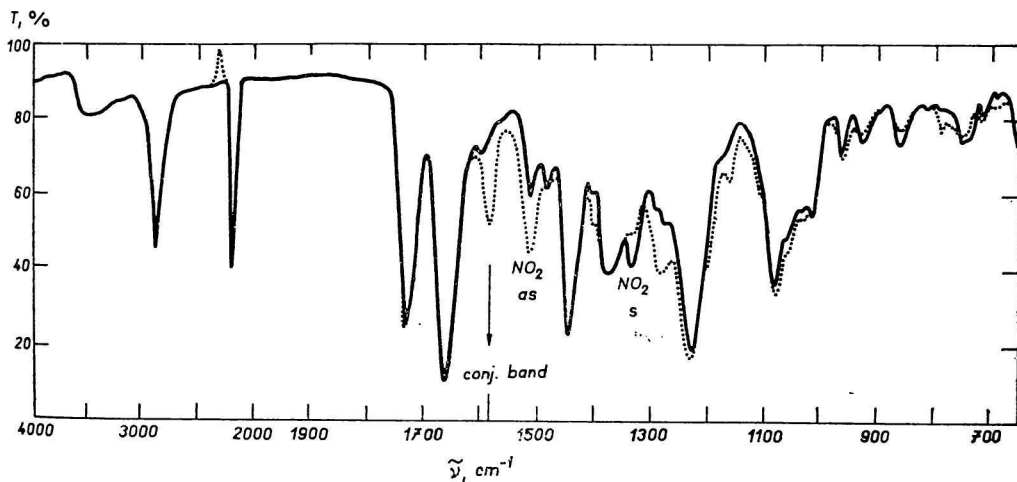


Fig. 1. Infra-red spectra of 1,3,3-trimethylindoline-6'-nitro-8'-bromobenzopyrylospirane in polyacrylonitril.

— colourless form
 coloured form

Observed spectra

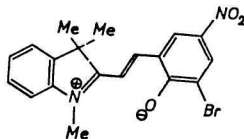
The spectra obtained for PAN thin films, SP + PAN thermal treated or irradiated, are shown in Fig. 1.

Discussion

As first approximation we will consider infra-red spectra of PAN + SP solid solution as the sum of the spectra of the individual components.

The interaction between unpolarized infra-red radiation and particular transition moment is a function of the component of that moment in a plane perpendicular to the direction of propagation of the radiation. When unpolarized infra-red radiation traverses a random arrangement of molecules (a gas, a liquid, or a powdered or amorphous solid) there is an equal probability of interaction between E -vector of the radiation and the transition moments associated with each of the various vibrational modes. However, this condition may not prevail when an anisotropic material (e.g. a single crystal, oriented sample or changeable structure of the molecules) is examined with unpolarized radiation. In this case it is possible for the transition moment arising from a given vibration to have a preferred orientation (parallel) to the direction of propagation of the radiation which would prohibit any absorption by that particular mode.

If we suppose the random orientation of SP planar molecule (coloured from) in PAN matrix, the changes of the infra-red spectra should belong to chemical changes in the course of the merocyanine \rightleftharpoons spiropyrane transformations. On the other side, in spite of the fact that in the preparation of the samples no special attention was paid to the orientation, we should keep in mind that PAN matrix strongly absorbs in infra-red region near 1670 cm^{-1} , belonging probably to a degraded structure of PAN and representing C=N vibration, which could have a preferred orientation. The diversity of existing hypotheses [2, 3] testifies to the lack of a definite view concerning the nature of the photo- and thermoreaction in this class of compounds, therefore it is difficult to interpret unequivocally several strong frequencies in the region $1600\text{--}650\text{ cm}^{-1}$, because of the presence of lines in the same region of the spectrum arising from different modes of vibration. In the region $1600\text{--}1500\text{ cm}^{-1}$ we observe two strong bands near 1590 and 1515 cm^{-1} belonging to SP molecule only (PAN does not absorb in this region). By irradiation with near ultraviolet ($\lambda = 3800\text{ \AA}$), visible ($\lambda = 6300\text{--}6900\text{ \AA}$), or with He+Ne laser beam of coloured merocyanic form, the photobleaching effect was observed and formation of SP structure is supposed. This effect is accompanied by the decrease of both above mentioned frequencies and a new strong band at about 1340 cm^{-1} frequency occurs. By thermal treatment or by irradiation with far ultra-violet the reversible increase of the absorption of both frequencies in the region $1600\text{--}1500\text{ cm}^{-1}$ and the decrease of the absorption near 1340 cm^{-1} occurred simultaneously. The process is reversible and reproducible.



Structure I

The strong reversible changes of infra-red absorption band near 1590 cm^{-1} in the photo- and thermochromism process are probably indicative of the C=O group of merocyanine form bonded to the conjugated system. Further the 1590 cm^{-1} band may be due to the vibration of C=N mode in the case of the structure I.

If the absorption band near 1590 cm^{-1} indicates C=O, or C=N group, its reversible changes, in dependence on wavelength of radiation or temperature, provide the proof for reversible spirane \rightleftharpoons merocyanine transformations.

The two bands at about 1340 and 1515 cm^{-1} belong, according to the results of various substituted spiropyranes, to stretching vibration of NO_2 group of SP molecule. Considering coplanar or non-coplanar SP molecule randomly oriented in PAN matrix we should find the probability of all possible vibrations roughly the same. In the case of coplanar structure (original sample, or after irradiation with far ultra-violet, or thermal treated), the absorption band at 1515 cm^{-1} assigned to the asymmetric stretching vibration appeared only. By irradiation with near ultra-violet, or intensive visible light, colourless form of SP was formed (non-coplanar with closed ring) and absorption band near 1340 cm^{-1} increased and near 1515 cm^{-1} decreased simultaneously. Francel [4] demonstrated the application of the polarized infra-red radiation in the study of the molecular structure of substituted nitrobenzenes. He assumed that in the compound under investigation the CN band is in the plane of the ring and collinear with a line bisecting the ONO angle. In the absence of steric effect (large substituents in *ortho* position) the nitro group would be expected to be coplanar with the ring. In case we want to observe just the asymmetric NO_2 vibration, the orientation of SP molecule should be perpendicular to the thin film plane and parallel to the *E*-vector. In the case that both frequencies near 1515 and 1340 cm^{-1} occur we assume that the part of SP molecule containing NO_2 group is located in the plane of the thin film.

On the basis of reversible changes of infra-red spectra in the region $650\text{--}1300\text{ cm}^{-1}$ due either to single bond stretching vibrations such as C—C, C—N or C—O bonds, or to the molecule structure itself, the assumption of stereochanges of SP molecule occurring in the course of thermo- and photochromism of SP, could be either corroborated or rejected. In general, the multiplicity of these absorptions is so great, and they are so strongly influenced by environment and the rest of the molecule, that their major value is in providing a spectrum characteristics of the molecule, rather than in the identification of the structural units.

The changes of the infra-red spectra belonging to PAN molecule only show a strong dipole-dipole interaction of SP and PAN molecules. Precise assignment of „sensitive“ frequencies will be studied and presented later.

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