PHOTO- AND THERMOCHROMIC SPIRANES.

25*. NEW INDOLINOSPIROPYRANS CONTAINING
A CONDENSED FURAN FRAGMENT

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New indolinospirochromenes have been synthesized containing a condensed furan fragment, an analog of the methoxyl substituent in position 6' of the chromene part of the molecule. Solutions of the obtained compounds display photochromic properties. For one of the compounds, depending on the temperature of irradiation, the cis-cisoid or trans-transoid isomer is fixed spectrally. An X-ray structural investigation has been carried out on crystals of spiropyrans possessing various forms of photoactivity in the solid phase.

Keywords: indolinospiropyrans, furan, X-ray structural analysis, photochromism.

The effect of substituents on the photochromic properties of spiropyrans has been studied previously, mainly on compounds containing various \(\pi\)-acceptor substituents [1-3]. The investigation of the effect of \(\pi\)-donor substituents is limited by their lack of variety, however it seems of particular interest since 6'-hydroxy-1,3,3-trimethylspiro(indolino-2',2'-[2H]-benzopyran) [4], and also indolinospirochromenes containing a methoxyl group in the 2H-chromene fragment [5], display photochromic properties in the solid phase.

A condensed furan fragment is an original replacement for the \(\pi\)-donor methoxyl group in position 6' of the spiropyran.

Spiropyrans 3b-d (Table 1) were obtained by a method analogous to that described previously for spiropyran 3a [6] by brief boiling in alcohol of equimolar quantities of 1,2,3,3-tetramethylindolenylium perchlorate 1, the appropriate aldehyde 2, and piperidine.

The IR spectra of compounds 3 contain absorption bands characteristic of the vibrations of the C=C bond of a pyran ring at 1600-1650 cm\(^{-1}\) (Table 2).

In the \(^1\)H NMR (CDCl\(_3\)) spectra of spirochromenes 3 signals were observed separately for the \(\text{gem}\)-dimethyl groups of the indoline fragment as a result of the acoplanarity of the molecule, but the doublet signal of the proton in position 3' of the pyran ring is characterized by a coupling constant of 8.6-10.6 Hz, which corresponds to a \text{cis} configuration for the vinyl fragment (Table 2).

* For Part 24 see [1].

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Compounds 3 display photochromic properties in solution. However, as a result of the short life time of the noncyclic isomers 4 under stationary conditions of irradiation, photocoloration is observed at temperatures below 250 K.

The cyclic isomers 3 are characterized by a long-wave structure-linked absorption at 330-380 nm (Table 3). At temperatures of 150-250 K, as a result of photoirradiation of solutions of compound 3, the appearance was observed in their absorption spectra of bands with a maximum at 585-625 nm, characteristic of the absorption of the noncyclic transoid isomers 4 (see Fig. 1 for the example of compound 3b). At lower temperatures (77 K) in the case of compound 3d the appearance of an absorption band is observed initially with a maximum at 471 nm, which on prolonged irradiation is transformed into a band with maximum at 585 nm (Fig. 2). The observed spectral changes are linked with the formation at the first stage of the cis-cisoid X-isomer 3', formed directly after fission of the Cspiro–O bond and is stabilized as a result of the steric manifestations of the bulky tert-butyl group and the viscosity barriers at low temperature, subsequent cis-trans photoisomerization leads to the appearance of transoid isomers 4.