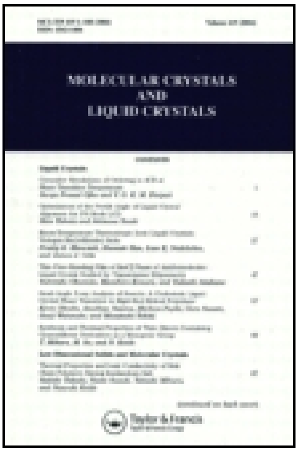

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The Structure and Photochromism of 3-Phenyl-5,5-dimethylspiro (1,3-oxazalidin-2-thione)-4,2′-[2H]chromenes

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THE STRUCTURE AND PHOTOCHROMISM OF 3-PHENYL-5,5-DIMETHYLSPIRO(1,3-OXAZALIDIN-2-THIONE)-4,2'-[2H]CHROMENES

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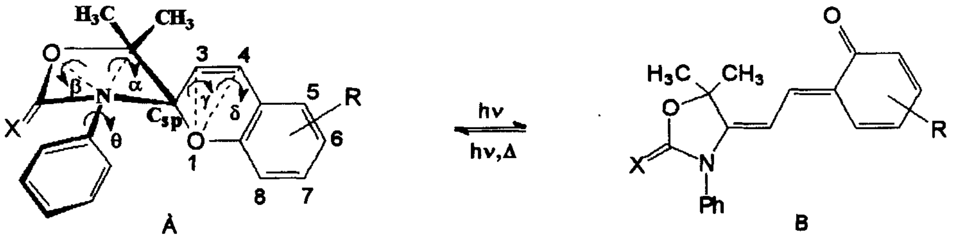
Abstract A series of novel spiropyrans, derivatives of 3-phenyl-5,5-dimethylspiro (1,3-oxazalidin-2-thione)-4,2'-[2H]chromene and its 2-oxo analogue have been synthesized and their photochromic properties studied. Molecular and crystal structures of four spiropyrans have been determined by X-ray crystal analysis.

INTRODUCTION

A correlation has been between the lengths of the C_{spiro}-O bond in spiropyrans derived on the basis of diverse heterocyclic cations or methylene bases and their proneness to the photochromic transformations due to cleavage of this bond in electronic excited state [1,2]. Only those spiropyrans were shown to exhibit photochromic behaviur for which the length of the C_{spiro}-O bond exceeded the value of 1.42 Å. In the present work the results of X-ray and photochemical studies of novel spiropyrans containing 2-thio-3-phenyl-5,5-dimethyl-1,3-oxazalidine moiety as a heterene fragment have been carried out in order to contribute to elucidation of the role of various structural factors which determine spectral and photochromic properties of spiropyrans.



I X=S, $R_8=NO_2$; II X=S, $R_6=OCH_3$; III X=S, $R_{5,6}$=benzo; IV X=O, $R_{5,6}$=benzo

EXPERIMENTAL

The spiropyrans **I-IV** were synthesized by the method described in [3]. The compounds **I** and **II** crystallize as colourless needles of monoclinic syngony and the compound **III** crystallizes as colourless needles of rombic syngony. The main crystal parameters are listed in Table 1.

TABLE 1. Main crystal data for spiropyrans **I-III**

Compound	Space group	a Å	b Å	c Å	γ,β°	d g cm^{-3}	Z
I	$P2_1/b$	8.037(8)	17.110(6)	14.026(7)	67.00(2)	1.386	4
II	Cc	11.750(6)	15.927(9)	9.710(7)	92.98(2)	1.256	4
III	$Pna2_1$	19.245(7)	12.728(5)	8.095(5)	90.00	1.258	4

The integral intensities of 1763 and 2200 independent reflections from crystals **I** and **III**, correspondingly, ($I>3\sigma$) were obtained on an automatic three-circle diffractometer DAR-UM (CuK_α-radiation). The integral intensities of 1490 independent reflections from crystal **II** have been obtained on an automatic four-circle diffractometer KM-4 (MoK_α-radiation). X-ray absorption in crystals was not accounted for. Structures were solved by a direct method using a complex of programs "Rentgen-75"[4] and "SHELX" [5] and refined by a full matrix least squares technique in anisotropic approximation.

The absorption spectra were recorded with a spectrophotometer "Specord UV-VIS" (Germany) equipped with a device for irradiation on the base of a 250 W high-pressure mercury lamp (DRSH-250), glass filters being employed. Efficiency of photocoloration (η) determined at 77 K in the mixture isopentane-isopropanol, (4:1) was estimated as the ratio of quantum yields of photocoloration of spiropyrans and 1',1',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indolin] 6-NO_2-BIPS by the method [6].

RESULTS AND DISCUSSION

All the spiropyrans **I-IV** exhibit photochromic properties due to reversible phototransformations **A** ↔ **B**. (Figure 1, Table 2).

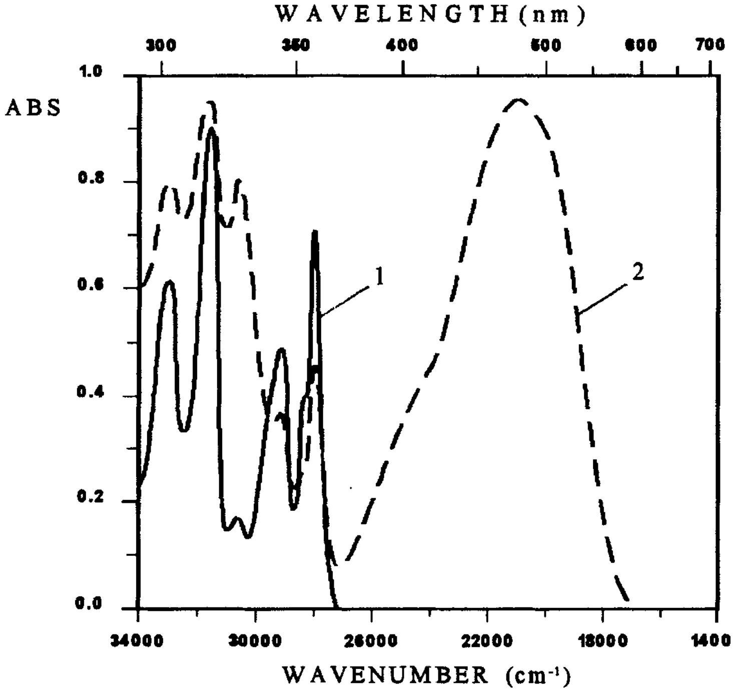


FIGURE 1. Absorption spectra of a spiropyran **III** in a rigid solution of isopentane-isopropanol (4:1) ($c = 6.8 \cdot 10^{-5}$ M, $T = 77$K) before (1) and after irradiation (365 nm) for 2400 s (2).

The longwave absorption band of the spirocyclic structures **A** is not significantly affected by the substituent in the chromene fragment, but undergoes a minor bathochromic shift on annelation to the chromene moiety of a benzene ring (the compound **III**). On the contrary, the annelation causes a noticeable hypsochromic shift of the longwave absorption band of the photocolored merocyanine isomer. This effect has been known for various other series of spiropyrans. When relatively weak effects of photo and thermal bleaching are neglected, the values of the photocoloration efficiencies (η) may be regarded as proportional to genuine quantum efficiencies of the photocoloration.

Table 2. Photochromic characteristics of the spiropyrans I-IV (isopentane-isopropanol 4:1, 77 K)

Compound	λ_{max}^{A}, nm	λ_{max}^{B}, nm	η
I	335	0	0
II	335	522	0.4
III	358	467	0.7
IV	360	475	0.3

For the studied compounds the values η decrease in the order of compounds **III**, **II**, **IV**, **I**. Table 3 contains some data on important bond lengths and angles in molecules **I-IV** as obtained by the X-ray crystal studies.

Table 3. Important structural parameters in molecules of spiropyrans I-IV

Compound	Bond length, Å		Angles degres					
	C_{sp}-O	C_{sp}-N	α	β	γ	δ	θ	φ
I	1.466	1.452	28.4	7.3	-3.4	-4.7	55.2	89.3
II	1.443	1.452	25.5	7.0	-15.3	-11.6	82.4	89.0
III	1.423	1.471	29.8	9.2	20.1	9.1	91.6	88.4
IV [8]	1.439	1.477	32.0	9.3	-22.8	-8.4	27.4	-

In all the compounds I - IV the length of the C_{spiro}-O bond is longer than the critical 1.42 Å magnitude, which fact is in agreement with the correlation [1,2] predicting their photochromic behaviour. The longest C_{spiro}-O bond found in the compound I (1.466Å) is, nevertheless, substantially shorter than those in indoline spyropyrans [2]. Another interesting structural feature of molecules of the spiropyrans I-IV is a noticeable

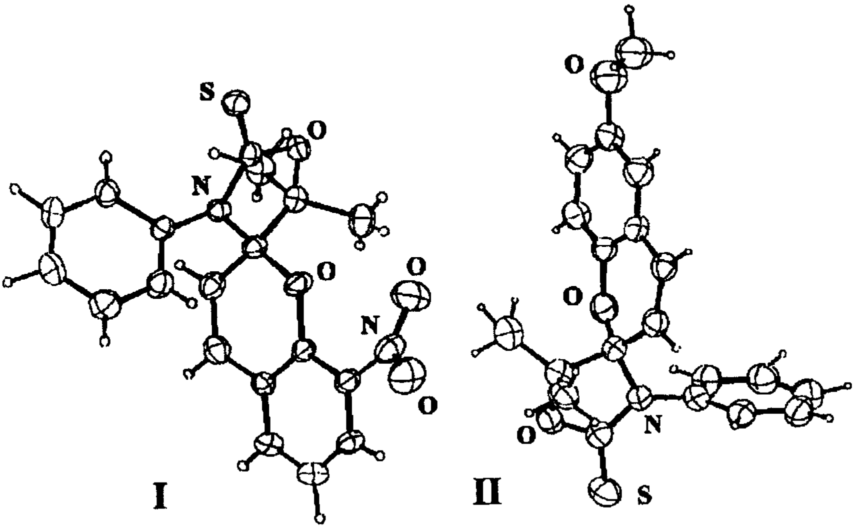


FIGURE 2. A stereoprojection of molecules I and II

puckering of both heterocyclic rings as indicated by the values of angles α–δ. Thus folding of 2H-chromene moiety along the C_3-O axis as measured by the corresponding dihedral angle γ achieves the value of 20°, which is larger than all previously reported values [2]. More detailed description of the molecular and crystal structures of the spiropyrans I-IV and some of their analogues will be given elsewhere

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