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PHOTOCHROMIC AND THERMOCHROMIC SPIRANES.
19.* 2-THIOXO-3-PHENYL-5,5-DIMETHYLSPIRO-(1,3-OXAZOLIDINE-4,2'-[2H]CHROMENES)

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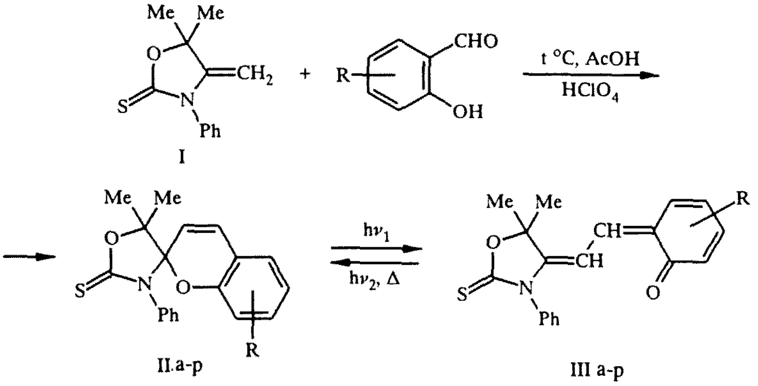
We have synthesized and characterized by IR, UV, ^1H, and ^{13}C NMR spectroscopy new spiropyrans based on 2-thioxo-3-phenyl-5,5-dimethyl-1,3-oxazolidine. We have studied their photochromic properties in 2-propanol at −80°C. In the electronic spectra of photo-induced forms, we have detected two long-wavelength absorption bands in the 370-438 and 480-677 nm region.

Continuing investigations on the effect of the nature of the heterocyclic component on the photochromic and thermochromic characteristics of spiropyrans, we synthesized the previously undescribed 2-thioxo-3-phenyl-5,5-dimethylspiro(1,3-oxazolidine-4,2'-[2H]chromenes) of type II.

The spiropyrans IIa-p (Table 1) were obtained in 50-70% yield by condensation of the methylene base I with *ortho*-hydroxyaromatic aldehydes in acetic acid, in the presence of catalytic amounts of perchloric acid.



I

II a-p

III a-p

In the IR spectra of compounds IIa-p (Table 2), we observe the characteristic $\nu_{C=C}$ absorption band of the pyran ring [2] at 1630-1670 cm^{-1} (medium intensity). The ^{1}H NMR spectrum of compound IIa, typical for this series of spiranes, is presented in Fig. 1. The signals from protons 3' and 4' are represented by an AB quartet with $\delta_{(3')} = 5.42$ and $\delta_{(4')} = 6.55$ ppm ($J_{3',4'} = 10$ Hz). Despite the achirality of structure II, the protons of the diastereotopic methyl groups at $C_{(5)}$ of the thioxooxazolidine ring are isochronous; and independently of the type of substituent R and the solvents used, ($CDCl_3$, $(CD_3)_2CO$) appear in the ^{1}H NMR spectra as singlet six-proton signals at 1.48-1.53 ppm (Table 3).

The isochronism of the methyl groups at the prochiral sp^3 atom in II observed in the ^{1}H NMR spectra may be due to the extremely small differences in the chemical shifts of the indicator signals $\Delta\delta < 0.3$ Hz ($f_0 = 100$ MHz) and/or realization in solutions of low-barrier ($\Delta G^{\neq} < 5$ kcal/mole) processes of thermally induced valence isomerism II $\rightleftharpoons$ III, leading to dynamic

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TABLE 1. 2-Thioxo-3-phenyl-5,5-dimethylspiro(1,3-oxazolidine-4,2′-[2H]chromenes) IIa-p

Compound	R	mp, °C	Found, %				Empirical formula	Calculated, %				Yield, %
			C	H	N	S		C	H	N	S	
II a	H	153 - 154	70,3	5,4	4,5	10,2	$C_{19}H_{17}NO_2S$	70,6	5,3	4,3	9,9	71
II b	5′,6′- Benzo	193 - 194	74,2	4,9	3,6	8,7	$C_{23}H_{19}NO_2S$	74,0	5,1	3,8	8,6	85
II c	6′,7′- Benzo	198 - 199	73,8	5,0	3,9	8,7	$C_{23}H_{19}NO_2S$	74,0	5,1	3,8	8,6	67
II d	7′,8′- Benzo	175 - 176	74,1	5,2	3,5	8,4	$C_{23}H_{19}NO_2S$	74,0	5,1	3,8	8,6	66
II e	6′-CH_3	113 - 114	71,0	5,8	4,0	9,7	$C_{20}H_{19}NO_2S$	71,2	5,8	4,2	9,5	77
II f	6′-NO_2	176 - 177	62,1	4,5	7,4	8,9	$C_{19}H_{16}N_2O_4S$	62,0	4,4	7,6	8,7	81
II g	8′-NO_2	181 - 182	61,8	4,6	7,5	8,5	$C_{19}H_{16}N_2O_4S$	62,0	4,4	7,6	8,7	67
II h	6′-OCH_3	170 - 171	70,5	5,7	4,3	9,6	$C_{20}H_{19}NO_3S$	70,4	5,6	4,1	9,4	91
II i	8′-OCH_3	148 - 149	70,5	5,7	4,3	9,5	$C_{20}H_{19}NO_3S$	70,4	5,6	4,1	9,4	84
II j	7′-OH	252 - 253	67,0	3,8	4,0	9,6	$C_{19}H_{17}NO_3S$	67,2	5,1	4,1	9,5	62
II k	6′-Cl*	103 - 104	63,6	5,4	4,1	8,8	$C_{19}H_{16}ClNO_2S$	63,8	5,4	3,9	9,0	95
II l	6′,8′-Cl_2*	197 - 198	58,3	4,0	3,4	8,4	$C_{19}H_{16}Cl_2NO_2S$	58,2	4,1	3,6	8,2	79
II m	6′-Br*	96 - 97	57,0	4,0	3,3	8,1	$C_{19}H_{16}BrNO_2S$	56,7	4,1	3,5	8,0	65
II n	6′,8′-Br_2*	192 - 193	47,4	3,3	3,1	6,4	$C_{19}H_{15}Br_2NO_2S$	47,4	3,1	3,0	6,7	72
II o	6′-Br,8′-NO_2*	247 - 248	51,0	3,5	6,4	7,0	$C_{19}H_{15}BrN_2O_4S$	51,0	3,4	6,3	7,2	72
II p	6′-NO_2,8′-Br*	239 - 240	51,3	3,5	6,1	7,3	$C_{19}H_{15}BrN_2O_4S$	51,0	3,4	6,3	7,2	83

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*Elemental analysis data for halogen correspond to the calculated values.

TABLE 2. Spectral Characteristics of Spiropyrans IIa-p

Compound	IR spectrum, ν, cm^{-1}	λ_{max}, nm (logε)	λ_{max} of photo-induced forms, nm in 2-propanol
II a	1646, 1600	255 (4,25), 297 shldr (3,29), 304 (3,51), 313 shldr (3,38)	376 shldr , 397, 511 shldr, 540, 575 shldr
IIb	1633, 1660	237 shldr (4,33), 241 (4,36), 252 shldr (4,15), 302 (3,51), 315 (3,60), 340 (3,34)	478
IIc	1646, 1600	250 shldr (5,05), 257 (5,11), 276 shldr (4,66), 289 (4,63), 302 (4,63)	380 shldr, 480
IId	1646, 1614	259 (4,55), 268 (4,62), 313 (3,55), 328 (3,51), 341 (3,42), 357 (3,39)	383, 469, 581 shldr
IIe	1633, 1600	255 (4,18), 314 (3,38)	377 shldr , 396, 500 shldr , 537
IIf	1646, 1612	262 (4,42), 303 (3,89)	533 shldr , 571
IIg	1636, 1622	254 (4,25), 327 (3,44)	396 shldr , 548, 597, 634
IIh	1633, 1598	252 (3,55), 331 (2,76)	374, 396, 520 shldr , 540, 586 shldr , 625 shldr
II i	1646, 1606	258 (3,63), 265 shldr (3,57)	396 shldr , 414, 545
II j	1620, 1593	258 (3,62), 265 shldr (3,57)	410, 438, 457, 494
II k	1689, 1646, 1620	253 (4,25), 316 (3,45), 325 shldr (3,38), 353 (3,08)	376, 396, 521 shldr , 552, 596, 645 shldr
IIl	1674, 1634	255 (4,34), 320 (3,41), 334 shldr (3,33)	387 shldr , 404, 533, 565, 609, 677
IIm	1669, 1640	255 (4,37), 314 (3,68)	376, 396, 516, 548, 591, 638 shldr
II n	1666, 1633	230 (4,85), 254 (4,30), 322 (3,42)	405, 533, 609, 660 shldr
IIo	1640, 1593	254 (4,31), 344 (3,38)	573, 608, 646
IIp	1646, 1606	252 (4,66), 262 shldr (4,62), 308 shldr (4,14), 316 (4,14)	410, 580

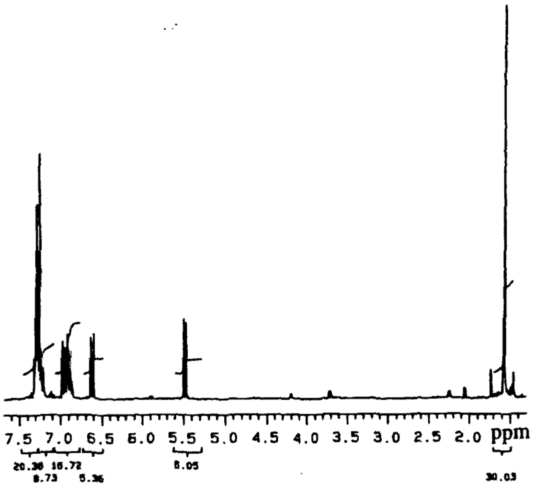

Fig. 1. ^{1}H NMR spectrum of spiropyran IIa in deuterochloroform.

averaging of the indicator signals due to inclusion of the achiral merocyanine structure III in the equilibrium. In fact, for spiranes of the indoline series very close in structure to II, containing geminal methyl groups which are practically as far from the stereogenic center as in II, the values of $\Delta\delta$ are 0.07-0.1 ppm, and the energy barrier ($\Delta G^{\neq}$) for thermochromic conversions "spiropyran ⇀ merocyanine" reaches 17-25 kcal/mole [3, 4].

Earlier it was shown [5] that the relative stability of spiropyran or merocyanine structures can be correlated with the anionic localization energy ($L^{\alpha}-$) of the corresponding carbon atom of the heterocyclic cation, on the basis of which the spiropyran system is formed. The equilibrium of the open and cyclic forms of spiropyrans is shifted more toward the latter as

TABLE 3. Characteristics of ^{1}H NMR Spectra of Spiropyrans IIa,b,f,h in $CDCl_3$ at 20°C, δ, ppm

Compound	R	$=C(CH_3)_2$ (6H, s)	3'-H, 1H, d ($^3J_{CH=CH'}$ Hz)	4'-H, 1H, d ($^3J_{CH=CH'}$ Hz)	Aromatic protons (m) (integrated intensity)
IIa	H	1,48	5,42 (10,0)	6,55 (10,0)	6,70 - 7,40 (9H)
IIb	5',6'-Benzo	1,55	5,97 (10,5)		Arom. protons + 4'-H 7,00 - 7,90 (12H)
IIf	6'-NO_2	1,53	5,66 (10,5)	6,65 (10,5)	6,90 - 8,20 (8H)
IIh*	6'-OCH_3	1,49	5,44 (9,0)		Arom. protons + 4'-H 6,30 - 7,30 (9H)

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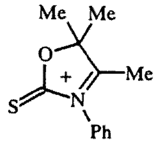
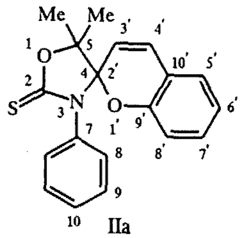
*IIh: 3.66 (2, 3H), 6'-OCH_3.

the anionic localization energy in the a position of the heterocyclic cation ($L^\alpha-$) becomes lower. The predominance of spiropyran structures can be expected for $L^\alpha- < 6.2$ eV, and the predominance of merocyanine structures can be expected for $L^\alpha- > 6.3$ eV (the ППП method in the Dewar σ, π parametrization).

The value of $L^\alpha- = 3.14$ eV calculated using this parametrization, determined for the 2-thioxo-3-phenyl-4,5,5-trimethyloxazolidinium cation IV, is significantly lower than the critical value (6.2 eV), below which we expect preferred existence in solution and in the solid phase of the spirocyclic form compared with the merocyanine form, and a value of $L^\alpha- = 4.46$ eV for the 1,2,3,3-tetramethylindolenylium cation.



IV



IIa

At the same time, in the ^{13}C NMR spectra of spiropyrans II, we note anisochronism of the carbons of the methyl groups in the 5 position of the thioxooxazolidine ring, the signals from which are observed separately at 20.38-21.06 and 23.07-23.43 ppm. The signals in the ^{13}C NMR spectra (Table 4) are assigned by comparing them with the structure of the original methylene base and using the data in [6, 7].

Upon irradiation with UV light with $\lambda_{max} = 313$ nm under steady-state conditions (DRSh-250 mercury lamp), the spiropyrans II undergo valence isomerization with formation of the corresponding [2-(6-oxacyclohexa-2,4-dienylidene)-ethylidene]-5,5-dimethyl-3-phenyl-2-thioxooxazolidines III and we observe reversibility of the photochromic properties.

The typical pattern for photochromic conversions is illustrated in Fig. 2 (for the example of compound IIa), and the spectral characteristics of the photochromism for other spiropyrans of this series are presented in Table 2. The long-wavelength absorption bands of the open forms III, absent before irradiation of IIa-p, are detected in the 370-438 and 480-677 nm region. SCF MO PPP calculations of the electronic spectra of the open forms III (for the example of IIIb) predict the presence of two long-wavelength absorption bands in the visible region of the spectrum, 376 and 514 nm. However, with the conventional parametrization of [5], in the experimental spectrum we observe a hypsochromic shift compared with the calculated spectrum.

TABLE 4. Characteristics of ^{13}C NMR Spectra of Spiropyrans IIIa,e-i and Starting Methylene Base I

N of C atom	I*	Compound/R					
		IIa	IIe*2	IIf	IIg	IIh*3	IIi*4
2	186,41	188,21	188,33	188,31	188,31	188,30	188,39
4	153,12	98,86	99,05	99,66	99,66	98,95	98,99
5	88,02	92,87	95,02	92,74	92,72	92,77	92,80
6	28,00	20,83 23,07	20,38 23,23	21,01 23,31	21,02 23,43	21,06 23,24	20,86 23,24
7	135,50	137,44	137,85	137,71	137,18	137,85	137,84
8	129,75	129,46	129,50	129,70	129,69	130,02	129,47
9	129,30	129,84	129,26	130,35	130,38	129,49	130,01
10	128,11	129,30	128,37	129,95	129,94	129,26	129,32
3′		115,65	115,48	122,35	118,29	116,57	119,92
4′		130,73	130,91	130,77	130,79	130,89	130,91
5′		128,01	124,26	126,40	130,60	119,06	116,77
6′		122,54	128,37	132,67	122,24	146,43	122,37
7′		131,34	129,77	130,17	126,39	130,89	114,64
8′		116,23	116,48	130,60	132,65	112,57	148,21
9′		152,27	150,46	145,45	145,46	155,36	141,58
10′		119,39	118,34	118,28	121,17	119,06	119,38

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*$\delta = \underline{C}H_2 = 84.14$ ppm.

*2IIe δ_6'-$\underline{C}H_3 = 21.02$ ppm.

*3 IIh δ_6'-$O\underline{C}H_3 = 55.92$ ppm.

*4 IIi δ_8'-$O\underline{C}H_3 = 56.56$ ppm.

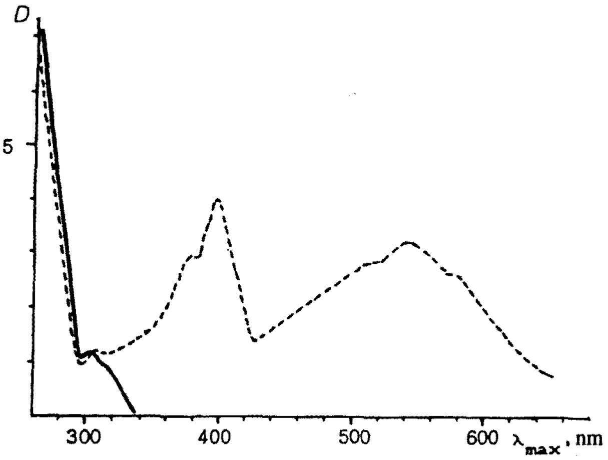


Fig. 2. Electronic absorption spectra of spiropyran IIa in 2-propanol at −80°C ($C \sim 5 \cdot 10^{-5}$ moles/liter, $l = 1$ cm) before (—) and after (---) irradiation.

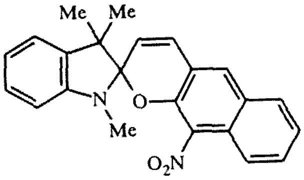
A comparative study of the absorption spectra of the open colored forms IIIa-p of the synthesized spiropyrans (Table 2) showed that introduction of π-acceptor (NO_2) substituents in the 6′ position (compounds IId,p) and π-donor (OCH_3) substituents in the 8′ position (compound IIi) causes a bathochromic shift of the long-wavelength absorption bands in the spectra of the photo-induced forms.

Benzoannelation at the 5′, 6′ positions of the chromene moiety of the molecule induces a hypsochromic shift of the long-wavelength absorption band of the photo-induced forms; and at the 7′, 8′ positions, a bathochromic shift.

For a number of practical purposes, it is especially important that the long-wavelength maximum of the absorption band of the colored form of spiropyrans be shifted as much as possible to the long-wavelength region of the spectrum. Calculations show that such a shift is possible in spiropyrans with linearly annelated rings (6,7-benzoannelation in the chromene moiety) [5]; and for spiropyran IIc, the position of the longest-wavelength maximum is ≈750 nm.

Generally spiropyrans with linearly annelated rings are difficult to obtain, but a product of this type could be synthesized in the thioxooxazolidine series (compound IIc). However, for this spiropyran, the longest-wavelength absorption band in the spectrum of the photo-induced form lies at 480 nm, i.e., the experimental transition energy differs from the calculated value by ≈1 eV.

The data we obtained are consistent with the results of [8]. It was shown that the long-wavelength absorption band of compound V appears as a low-intensity, smeared out absorption band in the 500-700 nm region. At the same time, the position of the absorption band in the 470 nm region is in good agreement with experiment (460-465 nm for compound V and 480 nm for compound IIc).



V

EXPERIMENTAL

The IR spectra were recorded on Specord IR-71 and Specord-75 double-beam spectrometers. The first beam was calibrated by taking the standard polystyrene spectrum. The samples were prepared in the form of a paste in vaseline oil or thin films obtained by evaporation of chloroform from the appropriate solutions on salt plates. The ^{1}H NMR spectra were recorded on a Tesla BS-487C instrument. The ^{13}C NMR spectra were taken on a Varian Unity 300 instrument (75 MHz) with full proton decoupling in the pulsed Fourier regime in deuteroacetone.

The electronic spectra of the investigated compounds before and after irradiation were recorded on a Specord UV-vis spectrophotometer fitted with a special cryostat. The operating temperature in the range 293-150 ± 1 K was achieved by regulated blowing of nitrogen around a cuvet placed in a quartz Dewar flask. The temperature was measured using a copper – constantan thermocouple and a digital voltmeter. As the exciting source, we used a DRSh-250 mercury lamp with light filters isolating light with λ_{max} 313 nm.

The spectral characteristics of the spiropyrans IIa-p obtained are presented in Tables 2-4.

2-Thioxo-3-phenyl-5,5-dimethyl(1,3-oxazolidine-4,2′-[2H]chromenes II. A mixture of 2.17 g (10 millimoles) methylene base I [9] and 11 millimoles of the corresponding orthohydroxyaromatic aldehyde were boiled for 1 h with a reflux condenser in a mixture of 20 ml AcOH and 3 drops of 70% $HClO_4$. After cooling, the reaction mixture was poured into 80 ml water and extracted (4 × 5 ml) with benzene. The combined extracts were washed with 5% $NaHCO_3$ and water, dried with anhydrous Na_2SO_4, and evaporated on a water bath under vacuum with a water aspirator pump to dryness. The residue obtained after driving off the solvent was recrystallized from alcohol with addition of activated charcoal, and IIa-p were obtained.

The yields, melting points, and elemental analysis data for compounds IIa-p are presented in Table 1.

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