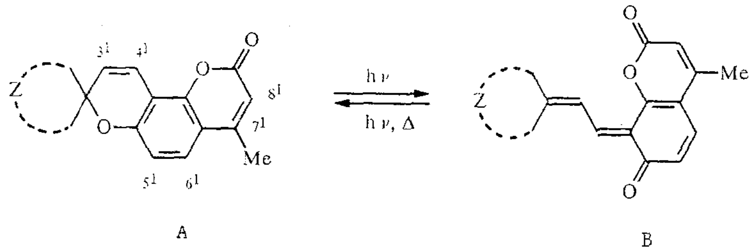
# PHOTOCHROMIC COUMARIN SPIROPYRANS

**V. V. Ivanitskii, O. G. Nikolaeva,**
**A. V. Metelitsa, N. V. Volbushko,**
**B. S. Luk'yanov, V. A. Palchkov,**
**and N. E. Shelepin**

*New photochromic spiropyrans (SPP) derived from 4-methyl-7-hydroxy-8-formylcoumarin have been synthesized. The effect of the heterene fragment on the spectral and photochromic properties of the SPP was examined. The photoproduct of the benzodithiolane SPP had the absorption with longest wavelength. Indoline SPP were found to have the most efficient photocoloring. Fluorescence of the cyclic form was found for the SPP.*

Hinnen [1] has reported the synthesis of an indoline spiropyran in the coumarin series. In a further study of the effect of the structure of the spiropyrans (SPP) on their spectral and photochemical properties, we synthesized spiropyrans I-XI, in which 4-methyl-7-hydroxy-8-formylcoumarin was used as the aldehydic component.



I - XI

I) Z = 1,3,3-trimethylindolenyl, II) Z = 1-propyl-3,3-dimethylindolenyl, III) Z = 1-hexyl-3,3-dimethylindolenyl, IV) Z = 1-octyl-3,3-dimethylindolenyl, V) Z = 1-benzyl-3,3-dimethylindolenyl, VI) Z = 2-oxo-3-phenyl-5,5-dimethyloxazolidenyl,VII) Z = 3,3-dimethyl-2-oxaindenyl,VIII) Z = 3-methyl-2H-1-benzopyrenyl, IX) Z = 3-methyl-2H-1-[2,1b]naphthopyrenyl, X) Z = 1,3-dithiolenyl, XI) Z = 5-methylbenzo-1,3-dithiolenyl

Products I-V were obtained upon heating equimolar amounts of the heterocyclic cation and formylcoumarin in ethanol at reflux in the presence of piperidine. Spiropyrans VII-XI were synthesized by the condensation of the corresponding heterocyclic perchlorates with the above-mentioned aldehyde in acetic acid in the presence of $HClO_4$ with subsequent treatment of the salts of the oxytriyl derivatives with ammonia in benzene. Product VI was obtained by heating equimolar amounts of the methylene base and formylcoumarin in glacial acetic acid at reflux in the presence of catalytic amounts of 70% perchloric acid.

The structures of these products were supported by their IR, PMR (Table 1), and UV spectra (Table 2).

The IR spectra of I-XI have bands for the coumarin carbonyl group at 1710-1750 $cm^{-1}$. The $C_{spiro}$—O bond gives rise to a band at 910-940 $cm^{-1}$, while the $\nu_{C=C}$ band of the pyran ring is found at 1610-1630 $cm^{-1}$.

The PMR spectra of I-XI have signals for the H-3' and H-4' ring protons at 5.45-6.2 ppm as doublets with J = 10 Hz, which are characteristic for spiropyrans (see Table 1). The second doublet of these protons is overlapped by multiplets belonging to the aromatic protons at 7.0-8.5 ppm, although this doublet is observed for VIII and X at 7.4-7.5 ppm. The position of the doublet for H-5' and H-6' at 6.5-7.0 ppm with J = 9 Hz is also characteristic. The second doublet is usually overlapped by the aromatic proton multiplet but is observed at 6.8-7.2 ppm for I, II, VI, and X.

---

Physical and Organic Chemistry Research Institute, Rostov State University, Rostov-on-the-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 601-604, May, 1992. Original article submitted November 21, 1989.

0009-3122/92/2805-0503$12.50

TABLE 1. PMR Spectra of Products in $CDCl_3$

| Compound | Chemical shift, δ, ppm | | | | |
|---|---|---|---|---|---|
| | heterene fragment | pyran fragment | | | |
| | | $C_{7'}$—$CH_3$ (3H, s) | $C_{3'}H$=$C_{4'}H$ (1H, d) ($J$=10 Hz) | $C_{8'}$—H (1H, s) | $C_{5'}H$—$C_{6'}H$ (1H, d) ($J$=9 Hz) |
| I | 1,17 (3H, s, C—$(CH_3)_2$), 1,30 (3H, s, C—$(CH_3)_2$), 2,73 (3H, s, N—$CH_3$) | 2,73 | 5,80 and 5,90 | 6,15 | 6,5 and 6,63,<br>6,84 and 6,93 |
| II | 1,14 (3H, s, C—$(CH_3)_2$), 1,26 (3H, s, C—$(CH_3)_2$), 0,84 (3H, t, $CH_2$—$CH_3$), 3,10 (3H, t, N—$CH_3$) | 2,34 | 5,75 and. 5,85 | 6,12 | 6,57 and 6,66,<br>6,81 and 6,90 |
| V* | 1,10 (3H, s, C—$(CH_3)_2$), 1,22 (3H, s, C—$(CH_3)_2$), 4,15...4,45 (2H, q, N—$CH_2$) | 1,60 | 5,45 and. 5,55 | 6,00 | 6,54 and 6,65 |
| VI | 1,38 (3H, s, C—$(CH_3)_2$), 1,45 (3H, s, C—$(CH_3)_2$) | 2,25 | 5,45 and. 5,55 | 6,00 | 6,75 and 6,87 |
| VII** | 1,70 (3H, s, C—$(CH_3)_2$), 1,80 (3H, s, C—$(CH_3)_2$) | 2,60 | 6,20 and 6,30 | 6,50 | 7,05 and 7,15 |
| VIII* | 1,82 (1H, s, C—$CH_3$) | 1,56 | 5,75 and 5,85,<br>7,40 and 7,50 | 5,92 | 6,62 and 6,66,<br>7,04 and 7,08 |
| IX* | 1,70 (1H, s, C—$CH_3$) | 1,40 | 5,50 and 5,60 | 5,65 | 6,40 and 6,50 |
| X | 3,40 and 3,65 (4H, t, $(CH_2)_2$) | 2,36 | 6,10 and 6,20,<br>7,40 and 7,50 | 6,18 | 6,80 and 6,90,<br>7,10 and 7,20 |
| XI | 2,2 (3H, s, C—$CH_3$) | 2,35 | 6,40 and 6,50 | 6,00 | 6,80 and 6,90 |

---

*Spectrum taken in $C_6D_6$.

**Spectrum taken in DMSO-$D_6$.

TABLE 2. Maxima of the Long-Wavelength Absorption for Fluorescence Excitation and of the Fluorescence of Spiropyrans I-XI and the Long-Wavelength Absorption of their Photoproducts

| Compound | $\lambda_{max}$, nm | | |
|---|---|---|---|
| | spiropyran | | photoproduct |
| | absorption (fluorescence excitation) | fluorescence | absorption |
| I | 350 (350) | 420 | 560 |
| II | 350 (350) | 420 | 560 |
| III | 350 | — | 562 |
| IV | 350 | — | 562 |
| V | 350 | — | 565 |
| VI | 345 (350) | 380 | 570 |
| VII | 330 | — | 600 |
| VIII | 328 (330) | 420 | 650 |
| IX | 346 (350) | 390 | 630 |
| X | 330 | — | 620 |
| XI | 350 | — | 660 |

**Note**: The absorption, excitation, and fluorescence spectra of the spiropyrans were taken in toluene at 293°K, while the absorption spectra of the photoproducts were taken in a mixture of isopentane and isopropyl alcohol at 193°K.

The protons of the coumarin methyl group at $C_{7'}$ give a three-proton singlet at about 2.3 ppm. The singlet at 6.0-6.15 ppm may be assigned to H-3'.

The electronic absorption spectra of I-XI show a long-wavelength band at 320-350 nm with pronounced vibrational structure typical for spiropyrans [2-4]. We note that the long-wavelength absorption maxima of oxaindane (VII), benzopyran (VIII), and dithiolane spirans (X) lie at shorter wavelengths (at 328-330 nm) than for the indoline (I-V), oxazolidine (VI), and benzodithiolane spiropyrans with $\lambda_{max}$ = 345-350 nm (see Table 2).

TABLE 3. Characteristics of Products Synthesized

| Compound | Mp. °C | Found, % | | | Chemical formula | Calculated, % | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N(S) | | C | H | N(S) | |
| I | 194...196 | 76,49 | 5,91 | 3,58 | $C_{23}H_{21}NO_3$ | 76,85 | 5,89 | 3,90 | 60 |
| II | 183...185 | 76,98 | 6,89 | 3,28 | $C_{25}H_{25}NO_3$ | 77,50 | 6,50 | 3,61 | 62 |
| III | 85...87 | 78,85 | 6,98 | 3,83 | $C_{28}H_{31}NO_3$ | 78,29 | 7,27 | 3,26 | 58 |
| IV | 73...75 | 81,03 | 5,21 | 3,48 | $C_{30}H_{35}NO_3$ | 80,51 | 5,63 | 3,13 | 56 |
| V | 210 | 79,31 | 6,20 | 3,54 | $C_{29}H_{25}NO_3$ | 79,98 | 5,79 | 3,22 | 60 |
| VI | 195...197 | 71,20 | 4,61 | 3,22 | $C_{23}H_{19}NO_5$ | 70,94 | 4,92 | 3,60 | 65 |
| VII | 230...231 | 75,98 | 5,41 | — | $C_{22}H_{18}O_4$ | 76,28 | 5,24 | — | 65 |
| VIII | 125...128 | 76,33 | 4,64 | — | $C_{22}H_{16}O_4$ | 76,73 | 4,68 | — | 55 |
| IX | 185...188 | 79,95 | 4,18 | — | $C_{26}H_{18}O_4$ | 79,18 | 4,60 | — | 54 |
| X | 240...243 | 58,78 | 4,50 | (20,68) | $C_{15}H_{20}O_2S_2$ | 59,19 | 3,97 | 21,07 | 60 |
| XI | 268...270 | 66,01 | 2,63 | (17,03) | $C_{20}H_8O_3S_2$ | 66,65 | 2,24 | 17,79 | 58 |

Spiropyrans I, II, VI, VIII, and IX have weak fluorescence at 380-420 nm (see Table 2). The fluorescence quantum yields of these compounds are less than $10^{-3}$.

Irradiation of solutions of spiropyrans I-XI in a 4:1 mixture of isopentane and isopropyl alcohol at 77-293°K at the long-wavelength absorption gives the thermally and photochemically reversible formation of acyclic, colored product B with characteristic absorption at 560-660 nm [2-4]. The position of the maximum of the long-wavelength band of photoproduct B depends significantly on the nature of the heterene part of the spiropyrans (see Table 2). The shortest wavelength for this band of photoproduct B is found for the indoline spiropyrans I-V ($\lambda_{max}$ = 560-565 nm), while the longest is found for benzodithiolane spiropyran XI ($\lambda_{max}$ = 660 nm).

The substituents at the nitrogen atom in the indoline part of I-V does not have a significant effect on the spectral indices of either the starting form A and photoproduct B or on the rate of photocoloring of the spiropyrans. We only note a slight increase in the thermal stability of photoproduct B in I-V, which is attributed to the bulk of the substituents at the nitrogen atom and the related steric hindrance to recyclization.

At 77°K, fluorescence was found for photoproduct B of I-V with $\lambda_{max}$ = 575-580 nm.

In regard to efficiency of photocoloring, indoline derivatives I-V are superior to VI and VII by about an order of magnitude and to VIII-XI by two orders of magnitude.

## EXPERIMENTAL

The electronic absorption spectra were taken on Specord M-40 and Specord UV-VIS spectrometers with an attachment for temperature control. The fluorescence and fluorescence excitation spectra were taken on a multipurpose Fotolyum instrument manufactured by the Central Construction Bureau of the Academy of Medical Sciences of the USSR. Homodyne detection permitting us to enhance sensitivity was used to record weak emissions. The photochemical studies were carried out using a DRSh-250 lamp and set of light filters to separate out the lines of the mercury spectrum. The photocoloring efficiency of I-XI was evaluated relative to the slope of the curve for $D/D_{max}$ vs. irradiation time for the point $t_{irr} = 0$ at $\lambda_{irr}$ = 313 nm (excitation to the second spiropyran singlet) and 193°K. The concentrations of the spiropyran solutions were taken such that the light incident on the cell at the outset was completely absorbed ($D_{(313\ nm)} = 2$).

The PMR spectra were taken on a Varian XL-100 spectrometer at 100 MHz with HMDS as the internal standard. The IR spectra were taken on a UR-20 spectrometer for vaseline mulls and $CCl_4$ solutions.

The parameters for the compounds synthesized are given in Table 3. The data for elemental analyses for C, H, N, and S corresponded to the calculated values.

**1,1′,3′,3′-Tetramethylspyro[3H,7H]-[benzo[1,2-b]-[3,4b′]-bipyran-7′,1-indoline]-3-one (I).** A mixture of 2.63 g (0.01 mole) 1,3,3-trimethylindolinium perchlorate, 2.1 g (0.011 mole) 4-methyl-7-hydroxy-8-formylcoumarin, and 0.1 g (0.001 mole) piperidine was heated in 20 ml ethanol at reflux for 1 h. The mixture obtained was poured into water and extracted with ether. The extracts were dried over sodium sulfate. Ether was evaporated to a minimum and the solution was passed through an alumina column using chloroform as the eluent. The solvent was evaporated off and the residue was recrystallized from ethanol. Products II-V were obtained by analogous procedures.

**1-Phenyl-3′,3′-dimethylspiro[3H,7H]-benzo[1,2b]-[3,4b′]bipyran-7′,1-oxazolidenin-2-one]-3-one (VI).** A mixture of 2.0 g (0.01 mole) 2-oxo-3-phenyl-4-methylene-5,5-dimethyloxazolindene-1,3 and 2.1 g (0.011 mole)

4-methyl-7-hydroxy-8-formylcoumarin was heated in 20 ml glacial acetic acid at reflux for 1 h. After cooling, the reaction mixture was poured into water and the precipitated product was filtered off. The purification of the product was carried out by analogy to the procedure for I.

**1,3′,3′-Trimethylspiro-[3H,7H]-[benzo[1,2b]-[3,4b′]-bipyran-7′,1-[2]-oxaindane]-3-one (VII).** A mixture of 2.6 g (0.01 mole) 1,3,3-trimethylisobenzofurylium perchlorate and 2.1 g (0.011 mole) 4-methyl-7-hydroxy-8-formylcoumarin in 20 ml acetic acid was heated at reflux for 15-20 min until a precipitate formed. After cooling, the precipitate was filtered off and washed with ether. A stream of dry ammonia was bubbled through a suspension of the perchlorate obtained in benzene until the precipitate became colorless and entered the solution. The benzene solution was filtered to remove the ammonium perchlorate precipitate and subjected to chromatography on an alumina column using chloroform as the eluent. The solution was evaporated and the residue was recrystallized from toluene.

Products VIII-XI were obtained analogously.

## LITERATURE CITED

1. A. Hinnen, French Patent No. 1,555,666; Ref. Zh. Khim., 7N755 (1970).
2. R. Heiligman-Rim, Y. Hirshberg, and E. Fisher, J. Phys. Chem., **66**, 2465 (1962).
3. M. Maguet, R. Guglielmetti, and F. Garnier, Nouv. J. Chim., **6**, 207 (1982).
4. S. M. Aldoshin, V. A. Lokshin, A. N. Rezonov, N. V. Bolbushko, N. E. Shelepin, M. I. Knyazhanskii, L. O. Atovmyan, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 6, 744 (1987).