

SYNTHESIS AND SOME PHYSICOCHEMICAL PROPERTIES OF
 6-NITRO-2H-CROMENE-2-SPIRO-2'-N-ALKYL-3',3'-
 DIMETHYLINDOLINES

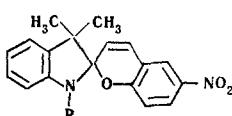
K. G. Dzhaparidze, D. P. Maisuradze,
 G. G. Gachechiladze, and É. S. Gomelauri

UDC 547.814'753.07

Indoline spirochromenes (spiropyrans) with various alkyl (C_2 – C_{10}) groups attached to the nitrogen atom were synthesized. The majority of them are photochromic in the crystalline state. The packing density of the spirochromene molecules in crystals decreases as the length of the alkyl groups attached to the nitrogen atom increases, and this explains the decrease in the melting points and the appearance of photochromic properties in the crystalline state.

In previous communications [1,2] we described the synthesis and physicochemical properties of some spirochromenes of the indoline series. In this paper we describe the synthesis of indoline spirochromenes containing a nitro group in the 6-position. The latter are readily obtained in neutral alcohol media by the condensation of 5-nitrosalicylaldehyde with the appropriate N-alkyl-2-methylene-3,3-dimethylindolines (homologs of the "Fischer base"). The reaction proceeds smoothly on heating, and the spirochromenes almost always precipitate from the mother liquors as rather pure crystals. They are quite soluble in the usual organic solvents and are characterized by clearly expressed thermochromic and photochromic properties (Table 1). Except for X, the dissolving of the colorless or light-yellow crystals of these compounds in polar solvents (particularly in alcohols) is accompanied by coloring of the solution. These compounds are colorless in the dark in hydrocarbon solvents and in polymer films, but they are colored λ_{max} in

TABLE 1



| Comp. | R | Mp | Found % | | | Empirical formula | Calcd. % | | | λ_{max} nm, in crystal | Sol. in alcohol, 20°, M · 10 ² | Yield, % |
|-------|----------------|---------|---------|-----|-----|----------------------|----------|-----|-----|---|---|-------------|
| | | | C | H | N | | C | H | N | | | |
| I | C_5H_5 | 157 | 71,4 | 6,0 | 8,5 | $C_{20}H_{20}N_2O_3$ | 71,4 | 5,9 | 8,3 | — | 2,42 | 87 |
| II | C_5H_7 | 135 | 72,3 | 6,6 | 8,1 | $C_{21}H_{22}N_2O_3$ | 72,0 | 6,3 | 8,0 | 580 | 1,60 | 66 |
| III | C_5H_9 | 100–101 | 72,3 | 6,7 | 7,6 | $C_{22}H_{24}N_2O_3$ | 72,5 | 6,6 | 7,7 | 590 | 4,75 | 70 |
| IV | C_5H_{11} | 81–82 | 72,9 | 7,1 | 7,3 | $C_{23}H_{26}N_2O_3$ | 73,0 | 6,9 | 7,4 | 600 | 5,61 | 83 |
| V | C_6H_{13} | 106 | 73,6 | 7,1 | 7,2 | $C_{24}H_{28}N_2O_3$ | 73,5 | 7,1 | 7,1 | 585 | 4,26 | 83 |
| VI | C_6H_{15} | 117–118 | 73,8 | 7,2 | 6,5 | $C_{25}H_{30}N_2O_3$ | 73,9 | 7,4 | 6,9 | 590 | 0,85 | 82 |
| VII | C_6H_{17} | 93–94 | 74,2 | 7,7 | 6,8 | $C_{26}H_{32}N_2O_3$ | 74,1 | 7,8 | 6,6 | 590 | 2,43 | 81 |
| VIII | C_6H_{19} | 75–76 | 74,5 | 7,7 | 6,7 | $C_{27}H_{34}N_2O_3$ | 74,6 | 7,9 | 6,5 | 590 | 2,44 | 83 |
| IX | $C_{10}H_{21}$ | 71–72 | 75,2 | 8,2 | 6,5 | $C_{28}H_{36}N_2O_3$ | 75,0 | 8,0 | 6,3 | 590 | 2,44 | 79 |
| X | C_6H_5 | 162–163 | 74,9 | 5,2 | 7,2 | $C_{24}H_{20}N_2O_3$ | 75,0 | 5,2 | 7,3 | — | 1,55 | 85 |
| XI | CH_3^* | 155–156 | 73,0 | 6,1 | 7,6 | $C_{22}H_{22}N_2O_3$ | 72,9 | 6,1 | 7,7 | 614 | 2,10 | 86 |

* In the pentamethylene 3-position.

Institute of Cybernetics, Academy of Sciences of the Georgian SSR, Tbilisi. Translated from Khimiya Geterotsiklicheskih Soedinenii, No. 6, pp. 775–777, June, 1971. Original article submitted November 18, 1969.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

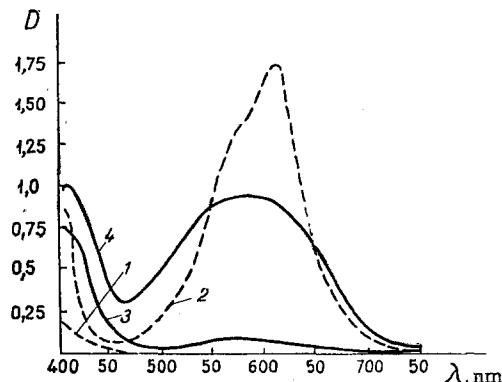


Fig. 1. Absorption spectra of 6-nitro-2H-chromene-2-spiro-2',1'-heptyl-3',3'-dimethylindoline (VI): 1,2) in toluene ($c 5 \cdot 10^{-5}$ M); 3,4) in the crystalline state; 1,3) before irradiation; 2,4) after irradiation.

lower in crystals of the spirochromenes than in solutions. The original state can also be restored by irradiation of the sample with visible light.

It is known that molecules are converted from a nonplanar to a planar configuration during photochromic transformations. Free rotation of the chromene portion of the molecule relative to the indoline ring is hindered during dense packing of the molecules in the crystals, and this also interferes with the manifestation of photochromism in the solid state. To confirm our assumption that an increase in the bulk of the substituents in the heterocyclic portion of indoline should induce a decrease in the packing density of the molecule in crystals, we synthesized 6-nitro-2H-chromene-2-spiro-2'-N-methylindoline-3'-spiro-1"-cyclohexane (XI), which is photochromic both in solutions (λ_{max} in toluene 575, 605 nm) and in the solid state. A decrease in the packing density of molecules in the crystals is accompanied by a decrease in the melting point and an increase in solubility.

EXPERIMENTAL

Spirochromenes (I-X, Table 1). A 2-g sample of the appropriate 2,3,3-trimethylindolenine alkiodide was decomposed with 5% aqueous alkali. The resulting oily liquid was extracted with ether, washed with water, and, after removal of the ether by distillation, dissolved in 30 ml of ethanol. An equimolecular amount of 5-nitrosalicylaldehyde was added to the alcohol solution, and the mixture was refluxed for 2 h. The mixture was cooled, and the resulting precipitate was filtered and crystallized from alcohol.

6-Nitro-2H-chromene-2-spiro-2'-N-methylindoline-3-spiro-1"-cyclohexane (XI). A mixture of 4.32 g (0.02 mole) of tetrahydroacetophenone phenylhydrazone, 11 g (0.08 mole) of anhydrous zinc chloride, and 15 ml of absolute ethanol was heated for 6 h. The mixture was cooled, treated with 20% aqueous potassium hydroxide, and extracted with ether. The ether extract was dried over potassium carbonate and fractionated with collection of the fraction with bp 180–187° (5 mm). Redistillation gave 1.3 g (32%) of 2-methylindolenine-3-spiro-1"-cyclohexane (XII). Found %: N 7.0. C₁₄H₁₇N. Calculated %: N 7.0. A 2-g (0.01 mole) sample of XII was heated in a sealed tube at 120° for 5 h with 2 g (an excess) of methyl iodide. After washing with amyl acetate and recrystallization from amyl acetate containing a few drops of ethanol, the crystals of the methiodide of XII melted at 218–219°. The yield was 0.95 g (68%). Found %: N 4.1; I 37.6. C₁₅H₂₀IN. Calculated %: N 4.1; I 37.2. Spirochromene XI was obtained as above from 2 g (~0.006 mole) of the methiodide of XII and 0.85 g (~0.006 mole) of 5-nitrosalicylaldehyde in 30 ml of ethanol.

LITERATURE CITED

1. D. P. Maisuradze, A. I. Nogaideli, and K. G. Dzhaparidze, Soobshch. Akad. Nauk Gruz. SSR. 49, 75 (1968); 50, 77.
2. K. G. Dzhaparidze, I. Ya. Pavlenishvili, M. T. Gugava, and D. P. Maisuradze, Zh. Fiz. Khim., 41, 582 (1970).

toluene 605 nm) after irradiation with UV rays (UFS-1 filter). The time required for spontaneous decoloration and the absorption maxima of the colored form in the visible region of the spectrum of an individual spiran vary as a function of the nature and character of the solvent. In contrast to N-alkyl compounds, the absorption maximum of the colored form of X is shifted to the long-wave side (λ_{max} in toluene 620 nm). This shift is caused by the inclusion of the benzene ring in the conjugated system of the colored form of the spiran.

Up to now, the reversible color change of spirochromenes was described only in the dissolved form, and photochromism was not noted in the crystalline state. The spirochromenes that we obtained [II-X (except for I, R = C₂H₅)] also display photochromic properties in the crystalline state. After irradiation with UV rays, the colorless or light-yellow crystals of these compounds acquire a blue coloration (Fig. 1). The rate of the dark reaction is much