

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

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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	Calc. %			λ_{max} nm, in crystal	Sol. in alcohol, 20°, M · 10 ²	Yield, %
			C	H	N		C	H	N			
I	C ₂ H ₅	157	71,4	6,0	8,5	C ₂₀ H ₂₀ N ₂ O ₃	71,4	5,9	8,3	—	2,42	87
II	C ₃ H ₇	135	72,3	6,6	8,1	C ₂₁ H ₂₂ N ₂ O ₃	72,0	6,3	8,0	580	1,60	66
III	C ₄ H ₉	100—101	72,3	6,7	7,6	C ₂₂ H ₂₄ N ₂ O ₃	72,5	6,6	7,7	590	4,75	70
IV	C ₅ H ₁₁	81—82	72,9	7,1	7,3	C ₂₃ H ₂₆ N ₂ O ₃	73,0	6,9	7,4	600	5,61	83
V	C ₆ H ₁₃	106	73,6	7,1	7,2	C ₂₄ H ₂₈ N ₂ O ₃	73,5	7,1	7,1	585	4,26	83
VI	C ₇ H ₁₅	117—118	73,8	7,2	6,5	C ₂₅ H ₃₀ N ₂ O ₃	73,9	7,4	6,9	590	0,85	82
VII	C ₈ H ₁₇	93—94	74,2	7,7	6,8	C ₂₆ H ₃₂ N ₂ O ₃	74,1	7,8	6,6	590	2,43	81
VIII	C ₉ H ₁₉	75—76	74,5	7,7	6,7	C ₂₇ H ₃₄ N ₂ O 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 ₂ O ₃	75,0	8,0	6,3	590	2,44	79
X	C ₆ H ₅	162—163	74,9	5,2	7,2	C ₂₄ H ₂₀ N ₂ O 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 ₂ O 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 Geterotsiklicheskikh Soedinenii, No. 6, pp. 775-777, June, 1971. Original article submitted November 18, 1969.

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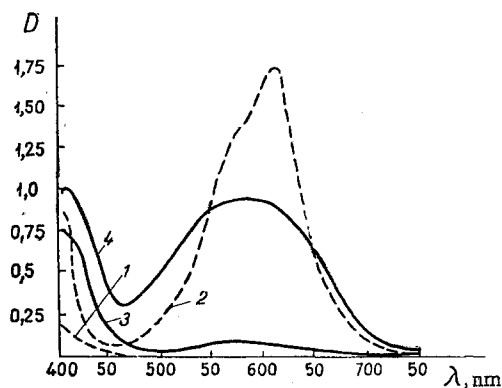


Fig. 1. Absorption spectra of 6-nitro-2H-chromene-2-spiro-2',1'-heptyl-3',3'-dimethylindoline (VI): 1,2) in toluene ($c \cdot 10^{-5}$ M); 3,4) in the crystalline state; 1,3) before irradiation; 2,4) after irradiation.

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. $C_{14}H_{17}N$. 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. $C_{15}H_{20}IN$. 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.

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