SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF 3'-NAPHTHYL-SUBSTITUTED BENZOTHIAZOLE SPIROCHROMENES

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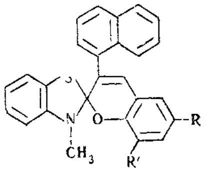
The condensation of 2-(α-naphthylmethyl)benzothiazole methiodide with salicylaldehyde derivatives in alkaline media gave 3'-naphthyl-substituted benzothiazole spirochromenes. Their photochromic properties were studied.

It is known that an electron-acceptor group (C_6H_5) in the 3' position promotes the stabilization of the "colored" form of benzothiazole spirochromene (spiropyran) [1, 2]. To establish the electronic and steric effects of substituents, we synthesized benzothiazole spirochromenes with a naphthyl group in the 3' position. The reaction of o-aminothiophenol and α-naphthylacetic acid yielded 2-(α-naphthylmethyl)benzothiazole, which was converted to 2-(α-naphthylmethyl)benzothiazole methiodide with methyl iodide. The corresponding spirochromenes (see Table 1) were obtained by the condensation of equimolar amounts of the quaternary salt and salicylaldehyde derivatives in alcohol in the presence of piperidine. All of them are soluble in alcohol, acetone, dioxane, dichloroethane, benzene, and toluene. In dioxane or dichloroethane, I and II give an intense violet color, but the color vanishes rapidly. In benzene and toluene, they give colorless solutions that have photochromic properties. This sort of behavior of these substances is apparently due to the steric effect of the naphthyl group. In all solvents except alcohol, III gives colorless solutions that have low-temperature photochromism.



A comparison of the absorption spectra of dioxane solutions of I and II demonstrated that λ_{max} at 445 nm of the colored solution vanishes during decolorization, and a new maximum appears at 275 nm. The absorption spectrum of III is characterized by λ_{max} at 305 nm in both dioxane and alcohol.

TABLE 1. 3'-Naphthyl-Substituted Benzothiazole Spirochromenes

Compound	R	R'	mp, °C (from alcohol)	Empirical formula	Found, %			Calc., %			Yield, %	Crystal color
					C	H	N	C	H	N		
I	NO_2	H	230—231	$C_{26}H_{18}N_2O_3S$	71,5	4,2	6,3	71,2	4,1	6,4	75	Dark-red
II	Cl	NO_2	214—215	$C_{26}H_{17}N_2O_3SCl$	66,2	3,5	5,9	66,0	3,6	5,9	72	Dark-red
III	H	OMe	224—225	$C_{27}H_{21}NO_2S$	76,4	4,9	3,4	76,6	4,8	3,3	67	Light-yellow

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EXPERIMENTAL

2-(α-Naphthylmethyl)benzothiazole [3]. A sealed tube containing 12.5 g (0.1 mole) of o-aminothiophenol and 37.2 g (0.2 mole) of α-naphthylacetic acid was heated at 180°C for 20 h. Aqueous potassium hydroxide was added to the reaction mixture until it was alkaline, and the mass that separated was extracted with ether. The ether was removed by distillation, and the residue was crystallized from ethanol to give 12 g (43.7%) of 2-(α-naphthylmethyl)benzothiazole with mp 70-71°.

2-(α-Naphthylmethyl)benzothiazole Methiodide. This compound was obtained by heating a mixture of 11 g (0.04 mole) of 2-(α-naphthyimethyl)benzothiazole and 23.4 g (0.2 mole) of methyl iodide in a sealed tube at 120° for 8 h. The crystalline, quaternary salt was removed by filtration, washed with acetone, and crystallized from ethanol to give 13.3 g (80%) of a product with mp 195-196°.

1-Methyl-3'-(α-naphthyl)-6'-nitrospiro[benzothiazoline-2,2',2'-n-chromene] (I). A mixture of 2.08 g (5 mmole) of 2-(α-naphthylmethyl)benzothiazole methiodide and 0.835 g (5 mmole) of 5-nitrosalicylaldehyde in 15 ml of ethanol containing 0.5 ml of piperidine was refluxed for 4 h and cooled. The precipitated spirochromene was removed by filtration, washed with ethanol, and crystallized.

LITERATURE CITED

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