(where R = CH_3, C_2H_5) the benzimidazole ring undergoes dealkylation. The resulting compound (II) is in all respects analogous to 6-amino-7-methylsulfonylbenzimidazo[1',2':1,6]pyrido[2,3-b]quinoxaline described in [1]. Here the alkyl group is eliminated as the corresponding alkyl chloride. This is unequivocally demonstrated by the formation of (III) by the reaction of chloro derivatives of (I) with 5,6-dihydroimidazo[i,j]quinoline.

With 1-phenylbenzimidazole there is formed the cyclic mesomeric betaine structure (IV) (cf. similar compounds in [2]). The retention of the phenyl substituent in the molecule, just as the detachment of the alkyl, corresponds to the thermal stability of the quaternary azolium salts [3].

Compounds (II-IV) were synthesized by boiling α-methylsulfonyl[2-(3-chloro)quinoxalyl]acetonitrile (I) with a twofold excess of the respective 1-substituted benzimidazole in c.p. dimethylformamide.

6-Amino-7-methylsulfonylbenzimidazo[1',2':1,6]pyrido-[2,3-b]quinoxaline (II). Mp >300°C. Yield 84% (R = CH_3) and 67% (R = C_2H_5). ??

4-(1-Chloro ??? Mp 229°C. PMR spectrum ($CDCl_3$, TMS): 2.35 (m, β-CH_2), 3.33 (t, γ-CH_2), 3.63 (t, α-CH_2), 3.74 (s, CH_3), 6.99 (s, NH), 7.4-7.7 (m, 2- and 3-H), 7.74-7.88 (m, 9- and 12-H), 8.13-8.27 (m, 10- and 11-H), 8.47 (s, NH), 9.01 ppm (d.d, J = 8.1 and 1.1 Hz, 1-H). Yield 61%.

5-Phenyl-7-methylsulfonylbenzimidazolium[1',2';1,6]-pyrido[2,3-b]quinoxaline-6-imidate (IV). Mp >30-0°. PMR spectrum (CF_3COOD, TMS): 3.72 (s, CH_3), 7.59 (d.d, J = 7.8 and 1.3 Hz, 4-H), 7.94-8.78 (m, 2-, 3-H, C_6H_5, 9-, 10-, 11-, 12H), 9.83 ppm (d.d, J = 8.1 and 1.2 Hz, 1-H). Yield 78%.

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NEW INDOLINE SPIROPYRANS WITH π-ACCEPTOR SUBSTITUENTS IN THE 8' POSITION

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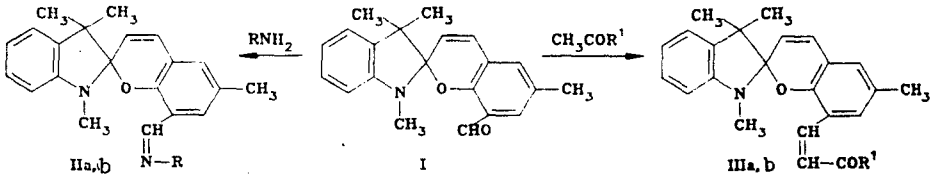
An important factor that determines the use of spiropyrans is the presence of the long-wave absorption of the photoinduced form, traditionally obtained by introducing a nitro group into the molecule [1]. It was of interest to use other π-acceptor substituents together with a lengthened photomeric cyanine conjugation chain.



II a R=4-$CH_3OC_6H_4$, b R=CH_2Ph; III a R^1=CH_3, b R^1=Ph

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We have therefore synthesized spirochromene (I) and from it, using the functionality of the formyl group, azomethines (II) and ketovinyl derivatives (III) (see scheme on page 1416).

Spiropyran (I) was obtained by boiling an equimolar mixture of Fischer base and 4-methyl-2,6-diformylphenol in alcohol for 2 h. Spiropyrans (II) are formed when (I) reacts in alcohol with an equimolar amount of the respective amine. Ketovinyl derivatives (III) are obtained by mixing equimolar amounts of (I) in alcoholic solution with the respective ketone and aqueous alkali.

Compound (I), mp 105-106°C (from alcohol), yield 56%. **Compound (IIa),** mp 173°C (from benzene–hexane), yield 61%. **Compound (IIb),** mp 155°C (from benzene–hexane), yield 36%. **Compound IIIa,** oil (purified by chromatography on Al_2O_3, with benzene), yield 62%. **Compound IIIb,** mp 137°C (from alcohol), yield 76%.

Elemental composition agreed with the calculated values.

The IR spectra of (I-III) contain intense absorption bands at 1650-1690 cm^{-1} (C=O or C=N), and a band at 1628-1655 cm^{-1} (pyran C=C).

The PMR spectrum of (IIa) shows an azomethine proton signal at 8.3 ppm; this is shifted more to the weak field than is the signal of the spiropyran formyl proton (9.99 ppm). In the spectra of (III) the doublet of the –CH=CH–CO– proton at 6.1-6.2 ppm ($^3J_{CH=CH}$ = 5-8 Hz) corresponds to the cis-configuration of the vinyl segment.

UV spectra (in propanol-2), λ_{max} (log ε): (I): 269 (4.14), 298 sh (3.66), 347 (3.60), 370 (3.62); (IIa): 232 (4.15), 285 (4.14), 326 (4.04), 340 sh (4.01), 381 (4.04); (IIb): 247 (4.28), 282 (4.43), 320 sh (3.54); (IIIa): 248 (4.33), 267 (4.24), 290 (4.27), 369 (3.75); (IIIb): 268 (3.99), 297 (3.87), 323 sh (3.75), 369 nm (3.93). The maxima of the long-wave bands of the photoinduced forms (irradiation with a DRSh-250 Hg lamp with 365 nm light filter under steady-state conditions, T ~ –70°C, c ~ $5 \cdot 10^{-5}$ mole/liter) were recorded in the electron spectra at 490 sh, 590 nm [for (I), (IIa, b), not photochromic; (IIIa), 628 nm; (IIIb), 615 nm].

Thus, when formyl is replaced by azomethine the photochromic properties disappear. The ketovinyl derivatives retain the photochromic properties; the maximum of the long-wave absorption band of their photoinduced forms is shifted bathochromically by 25-40 nm in comparison with starting spiropyran (I).

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