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LETTERS TO THE EDITOR

NOVEL UNSYMMETRICAL PHOTOCHROMIC 2,3-DIHYDRO-4-OXONAPHTHO[2,1-*e*][1,3]-OXAZINE BISPIROPYRAN

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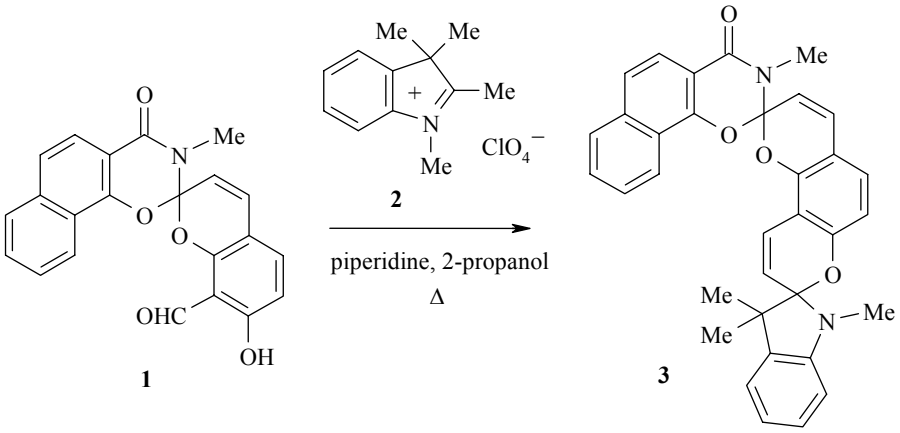
The photochromic properties of spiropyrans are determined by the contribution of the hetarene fragment and the substituents in the 2H-chromene part of the molecule [1]. We have prepared the previously unknown spiropyran **1** which contains a condensed benzo ring in the benzoxazine fragment as an unusual analog of salicylic aldehyde. From this we have synthesized the unsymmetrical bispiropyran **3** which has two different spirocyclic centers and, hence, two asymmetric carbon atoms.



The ^{1}H NMR spectra were taken on a Varian Unity-300 (300 MHz) instrument using the residual proton signals of the deuterated solvent ($CDCl_3$) as standard at 7.26 ppm

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8'-Formyl-7'-hydroxy-3-methylspiro(2,3-dihydronaphtho[2,1-*e*][1,3]oxazine-4-oxo-2,2'-[2H]chromene) (1) was prepared by a previously reported method [2] from N-methylsalicylamide and 2,4-dihydroxyisophthalic aldehyde. Yield 48%, mp 191°C (ethanol). IR spectrum (thin film), ν, cm^{-1}: 1673 (C=O), 1647, 1593 (C=C), 973 (C–O). UV spectrum (2-propanol), λ_{max}, nm (log ε): 328 (3.68), 343 (3.83). ^{1}H NMR spectrum, δ, ppm (J, Hz): 3.22 (3H, s, N-CH_3); 6.07 (1H, d, *J* = 10.0, H-3'); 6.60 (1H, d, *J* = 8.5, H-6'); 7.01 (1H, d, *J* = 9.6, H-4'); 7.37-7.45 (2H, m, H-5',9); 7.51-7.64 (2H, m, H-8,10); 7.83 (1H, d, *J* = 8.1, H-7); 7.96 (1H, d, *J* = 8.5, H-6); 8.03 (1H, d, *J* = 8.5, H-5); 9.78 (1H, s, CHO); 11.64 (1H, s, OH). Found, %: C 70.66; H 3.94; N 3.64. $C_{22}H_{15}NO_5$. Calculated, %: C 70.77; H 4.05; N 3.75.

1'',3'',3'',3-Tetramethyl-4-oxo-2,3-dihydronaphtho[2,1-*e*][1,3]oxazine-2-spiro-2'-2H,8H-pyrano[2,3-*f*]-chromene-8'-spiro-2''-indoline (3). Piperidine (0.1 ml, 1.1 mmol) was added dropwise with heating to a solution of the spiropyran **1** (0.383 g, 1 mmol) and 1,2,3,3-tetramethylindolenium perchlorate (**2)** (0.274 g, 1 mmol) in 2-propanol (5 ml). The reaction mixture was refluxed for 10 min and cooled. The precipitate was filtered off and recrystallized from hexane.

Yield 0.287 g (53%), mp 210°C (hexane). IR spectrum (thin film), ν, cm^{-1}: 1673 (C=O), 1633, 1607 (C=C), 972 (C–O). UV spectrum (2-propanol), λ_{max}, nm (log ε): 327 (3.88); 342 (3.87), λ_{max} of the photoinduced form 507 and 613 nm (steady state irradiation activated by Σ mercury lamp light (DRSh-250). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.03 (3H, s, 3''-CH_3); 1.10 (3H, s, 3''-CH_3); 2.43 and 2.63 (3H, 2s, 1''-CH_3); 3.22 (3H, s, 3-CH_3); 5.39 (1H, d, *J* = 10.4, H-9'); 5.98 (1H, d, *J* = 9.6, H-3'); 6.36-6.50 (2H, split, m, H-5',6'); 6.62 (1H, d, *J* = 10.4, H-10'); 6.80 (1H, t, *J* = 7.3, H-6''); 6.93-7.04 (3H, split. m, H-4',4'',7''); 7.12 (1H, t, *J* = 7.7, H-5''); 7.30-8.11 (6H, split. m, H-5,6,7,8,9,10). Found, %: C 77.39; H 5.27; N 5.21. $C_{34}H_{28}N_2O_4$. Calculated, %: C 77.25; H 5.34; N 5.30.

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