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LETTERS TO THE EDITOR

A NEW SPIROPYRAN WITH A CATION RECEPTOR

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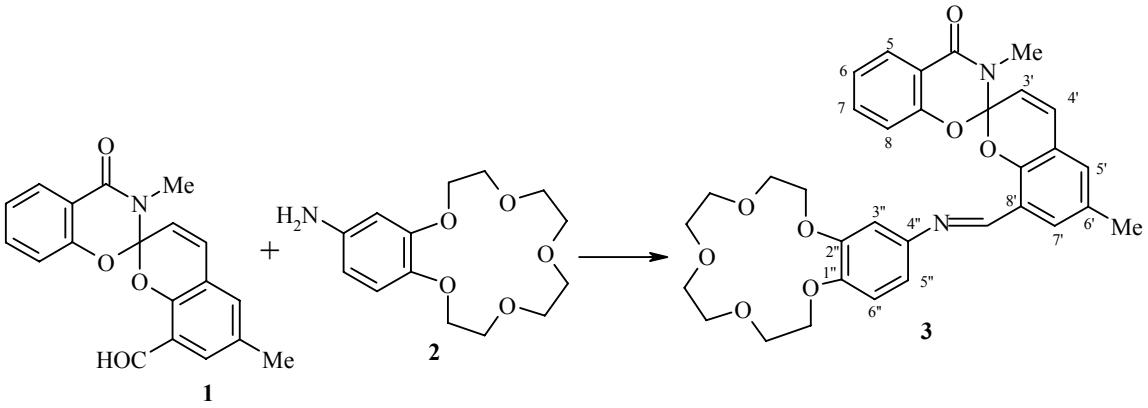
A new spiropyran **3** with a cation receptor was synthesized in a study on the introduction of photo- and chemosensor substituents capable of selectively fixing metal ions [1]. The benzocrown-5 fragment in **3** was connected to the benzo unit of a [2H]-chromene fragment through a conjugated π-electron-withdrawing C=N bond in order to enlarge the conjugation chain in the open colored form.



Upon the possible capture of a metal ion by the crown ether cavity, the complex formed might be a unique additional π-electron-withdrawing substituent, which, as shown in our previous work [2], activates photochromic properties in spiropyrans containing an azomethine substituent. However, we unexpectedly found that colored merocyanine products are not formed upon photoirradiation of spiropyran **3** at 365 nm. Only reversible *E-Z* isomerization of the C=N bond (τ_{30} = 5.1 sec) was observed. The introduction of lithium ions into a solution of spiropyran **3** even in a 30-fold excess did not lead to the appearance of photochromic properties in the system studied in contrast to indoline spiropyrans [3].

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The ^{1}H NMR spectra were taken on a Varian Unity 300 spectrometer at 300 MHz in $CDCl_3$. The signals were assigned relative to the signals of the residual protons of the deuterated $CDCl_3$ solvent at 7.26 ppm. The IR spectra were taken on a prismatic two-beam Specord IR-7 spectrometer for vaseline mulls. The spectrometer was calibrated relative to polystyrene. The UV spectra were taken on a Cary Varian spectrophotometer. A DRSh-250 mercury lamp with light filters emitting light with λ_{max} = 313 and 365 nm was used as the excitation source.

8'-(3-Iminobenzo-15-crown-5)-3,6'-dimethyl-4-oxo--3,4-dihydrospiro(2H-1,3-benzoxazine-2,2'-[2H]-chromene) (3). 4-Aminobenzo-15-crown-5 **2** [5] (0.09 g, 0.031 mmol) was added to a solution of 8'-formyl-3,6'-dimethyl-4-oxo-3,4-dihydrospiro(2H-1,3-benzoxazine-2,2-[2H]-chromene) **1** (0.1 g, 0.3 mmol) obtained according to our previous procedure [4] in ethanol (3 ml) at reflux. The solution was heated at reflux for 30 min. The solvent was distilled off in vacuum and the residue obtained was recrystallized from ethanol to give 0.15 g (81%) **3**, mp 153-154°C. IR spectrum, ν, cm^{-1}: 1680 (C=N), 1642 (C=O), 1617, 1578 (C=C), 1264 (C–N), 1148, 974, 952 (C–O). UV spectrum in acetonitrile, λ_{max}, nm (ε): 240 (34,500), 262 sh (28,690), 358 (14,910). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.35 (1H, s, CH_3); 3.19 (1H, s, N–CH_3); 3.64-4.18 (16H, m, O–CH_2–CH_2–O); 6.12 (1H, d, *J* = 9.7, H-3'); 6.39 (1H, dd, *J* = 8.5, *J* = 2.3, H-5"); 6.54 (1H, d, *J* = 2.3, H-3"); 6.74 (1H, d, *J* = 8.5, H-6"); 6.84 (1H, d, *J* = 8.0, H-8); 7.00 (1H, d, *J* = 9.7, H-4'); 7.10-7.20 (2H, m, H-6, H-5'); 7.43 (1H, m, H-7); 7.86 (1H, m, H-7'); 8.04 (1H, d, *J* = 7.8, H-5); 8.26 (1H, s, N=CH). Found, %: C 67.42; H 5.93; N 4.65. $C_{33}H_{34}N_2O_6$. Calculated, %: 67.56; H 5.84; N 4.78.

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REFERENCES

1. O. A. Fedorova, S. P. Gromov, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.***,** 1882 (2002).
2. B. S. Lukyanov, L. E. Nivorozhkin, and V. I. Minkin, *Khim. Geterotsikl. Soedin.*, 176 (1993) [*Chem. Heterocycl. Comp.*, **29**, 152 (1993)].
3. M. V. Alfimov, A. V. Balakin, S. P. Gromov, Yu. V. Zaushitsyn, O. A. Fedorova, N. I. Koroteev, A. V. Pakulev, Yu. V. Rossiyatnskii, and A. P. Shkurinov, *Zh. Fiz. Khim.*, **73**, 1871 (1999).
4. B. B. Safoklov, B. S. Lukyanov, A. O. Bulanov, A. V. Metelitsa, V. I. Minkin, V. V. Tkachev, and S. M. Aldoshin, *Izv. Akad. Nauk, Ser. Khim.*, 431 (2002).
5. R. Ungaro, B. E. Haj, and J. Smid, *J. Am. Chem. Soc.*, **98**, 5198 (1976).