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Syntheses of Some Arylazospiropyran

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The 6-(4-nitrophenylazo), 5'-chloro 6-(4-nitrophenylazo), and 5'-(4-fluorophenylazo)-
derivatives of 1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] were synthesized and
their structures were assigned by their ¹H- and ¹³C-NMR spectral data.

Benzospiropyranäs in solution are interconvertible between two tautomers; a non-polar spiropyran-
and a dipolar merocyanine form, by way of a thermal or a photochemical process, where the
witter-ionic merocyanine form is dominant over the tautomeric counterpart in a polar solvent. Such
preference is enhanced by introducing an electron-withdrawing substituents to the benzopyran moiety,
as can be observed in the tautomerism of 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (1)ë.

We have investigated the arylazo group as an electron-withdrawing substituent on a spiropyran
skeleton with the purpose of attaining an enhanced bathochromic shift upon the isomerization of the
molecule to the merocyanine form, caused by dipolar interactions of the dye molecule with neighboring
molecules. So far very few arylazo derivatives of benzospiropyran have been reported in the literature,
6-(4-nitrophenylazo) (2)ë and 8-(arylazo)-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline]ţ being the
exceptions. This paper describes the syntheses and characterization of 5'-(4-fluorophenylazo) (3),
5'-chloro 6-(4-nitrophenylazo)-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (4) and some reference
compounds for the use in spectral measurements.

Results and Discussion

The azo-coupling reaction of 1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (5) with
4-fluorobenzenediazonium ion under phase-transfer catalyzed conditionsë occurs exclusively at the
5'-position of its indoline moiety, to afford arylazobenzospiropyran 3 in an excellent yield of more than
90% [Scheme 1], while no substitution was observed at the 6-position of its benzopyran moiety. Such a
high selectivity is readily understandable, because the 5'-position of the indoline moiety is para to a

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mesomeric electron-donating alkylamino substituent. High reactivity at the 5'-position was observed also in a reaction with the less reactive nitrosating agent; the nitrosation of benzospipyran 1 under phase-transfer catalyzed conditions\(^8\) afforded 5',6-dinitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (6)\(^l\) as the only definite product [Scheme 2], though its yield being not very high, where the final product 6 was regarded to be formed by the consecutive nitrous-acid oxidation of the initially formed 5'-nitroso product under the reaction conditions.\(^6\)

When the azo-coupling reaction is carried out in acid media, where benzospipyran is isomerized to a dipolar merocyanine form, the 5-position in its 2-hydroxyphenyl moiety may be expected to be more susceptible to an electrophilic attack than the 5'-position in its indolino one due to the former \textit{para} to an electron-releasing oxylato group and the latter \textit{para} to an electron-attractive ammonio one. In practice, the azo coupling of 5'-chloro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (7)\(^8\) with 4-fluorobenzenediamonium ion afforded no product at all in an acetic acid solution in the presence of sodium acetate, and the starting 5'-chlorobenzo-spiropyran 7 was recovered almost quantitatively.

Under the phase-transfer catalyzed conditions by use of TFPB, the reaction with the same reactants gave a complex mixture, from which the desired 5'-chloro-6-(4-fluorophenylazo)-1',3',3'-trimethylspiro-[2H-1-benzopyran-2,2'-indoline] was difficult to be isolated.

The introduction of an arylazo group on to the benzopyran moiety could be achieved in a usual
manner" [Scheme 3] by the condensation of 5-chloro-1,3,3-trimethyl-2-methyleneindoline (8) with a salicylaldehyde derivative (9) which was 4-nitrophenylazo-coupled in advance at the position para to its hydroxyl group. The reaction proceeded readily to afford the 6-(4-nitrophenylazo)spiropyran 4 in 59% yield. Similar condensation of 1,3,3-trimethyl-2-methyleneindoline (10) with 9 also afforded the corresponding arylazobenzospiropyran 2 in a good yield.

Elemental analyses, and mass- and NMR spectral data are compatible with the assigned structures of products. The details of assignments of "H- and "C-NMR signals and solvatochromism of these arylazobenzospiropyrans will be described elsewhere.

Experimental

Instruments and reagents: NMR spectra were obtained on a JEOL JNM-FX-100 spectrometer at 99.6 and 93.65 MHz for "H- and "F nuclides, respectively, and on a JNM-EX-270 one at 270.16 MHz for "H and at 67.94 MHz for "C as proton wide-band decoupled spectra. Chemical shifts are reported for deuterochloroform solutions in ppm positive downfield from internal TMS for "H- and "C-NMR and from internal hexafluorobenzene for "F-NMR spectra, unless otherwise stated. When required for higher-resolution measurements, NMR spectra were recorded on a JEOL JNM-GSX-500 instrument at 500.16 and 125.77 MHz for "H- and "C nuclides, respectively. Mass spectra were recorded on a JEOL-JMS-01SG-2 mass spectrometer. 4-Fluorobenzenediazonium+, and 4-nitrobenzenediazonium tetrafluoroborates, spirobenzopyrans 1 and 5, intermediates 8, 9, and 10, were commercially available reagents and used after purified by appropriate methods.

Syntheses:

6-(4-Nitrophenylazo)-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (2) : 1,3,3-Trimethyl-2-methyleneindoline (8) (33 mg, 0.19 mmol) was added into a hot methanol solution of 5-(4-nitrophenylazo)-salicylaldehyde (9) (51 mg, 0.19 mmol / 20 ml), and the resulting solution was heated under reflux for 8 hr. After cooled to room temperature, a resulting solid precipitate was collected by filtration to give orange crystals of 2 (62 mg, 76% yield). The crystal liquidizes once at 205 ~ 206°C, then solidifies upon
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continuing to heat, and finally melts at 215°--216°C (lit.9; mp. 205 ~ 206°C). Anal.: Found; C, 70.18; H, 5.30; N, 12.81%. Calcd. for CsH25N2O: C, 70.41; H, 5.20; N, 13.14%. 'H NMR: δ ; 8.38 (dt, J = 2.5, 8.9 Hz, 2H), 7.80 (dd, J = 2.3, 8.9 Hz, 1H), 7.74 (d, J = 2.3 Hz, 1H), 7.20 (br-t, J = 7.6 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 6.97 (d, J = 10.2 Hz, 1H), 6.88 (t, J = 7.3 Hz, 1H), 6.85 (d, J = 8.6 Hz, 1H), 6.56 (d, J = 7.9 Hz, 1H), 5.82 (d, J = 10.2 Hz, 1H), 2.77 (s, 3H), 1.33 (s, 3H), and 1.20 ppm (s, 3H).13C NMR: δ ; 158.6, 156.0, 148.1, 147.9, 146.5, 136.4, 129.0, 127.7, 126.5, 124.7, 123.0, 121.7, 121.5, 120.8, 119.5, 119.1, 107.0, 105.7, 52.1, 28.9, 25.9, and 20.0 ppm.

1',3',3'-Trimethyl-5'-(4-fluorophenylazo)spiro[2H-1-benzopyran-2,2'-indoline] (3) : Into a two-phase mixture of a dichloromethane solution of 1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (5) (279 mg, 1.00 mmol/20 ml) and an aqueous buffer solution of 4-fluorobenzenediazonium tetrafluoroborate (212 mg, 1.01 mmol/50 ml) was added sodium TFPB 10 (174 mg, 0.187 mmol), and the mixture was stirred vigorously for 3 hr at room temperature. Azo-coupling reaction proceeded in the two-phase system. A solid residue (720 mg), which was separated from the red-colored dichloromethane layer of the reaction mixture after usual work-up, was chromatographed on a silica gel column. An initially eluted fraction upon developed with chloroform gave a yellow solid, which was recrystallized from a dichloromethane-hexane mixture to afford yellow crystals 3, mp. 208°C (364 mg, 90% yield). Anal.: Found; C, 75.40; H, 5.73; N, 10.15%. Calcd. for C25H22N30F; C, 75.17; H, 5.55; N, 10.52%. UV (dichloromethane) : λmax; 396 nm (ε = 2.86 × 104). MS: m/z (relative intensity); 400 (28), 399 (M+, 100), 398 (11), 384 (25), 276(10), 158 (47), and 95 (11). Accurate m/z: Found; 399.1748. 19F NMR: δ ; 49.9 ppm (tt, J = 8.2, 5.2 Hz).13C NMR: δ ; 163.5 (d, ΔJCF = 250 Hz), 154.1, 151.0, 149.6 (d, ΔJCF = 4 Hz), 146.7, 138.0, 130.0, 129.8, 128.6, 126.8, 124.6 (d, ΔJCF = 9 Hz), 120.4, 118.5, 118.5, 115.8 (d, ΔJCF = 23 Hz), 115.0, 113.7, 106.1, 104.2, 51.4, 28.9, 25.8, and 20.2 ppm.

5'-Chloro-6-(4-nitrophenylazo)-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (4) : 5-Chloro-1,3,3-trimethyl-2-methyleneindoline (10) (213 mg, 1.03 mmol) was added into a hot methanol solution of 5-(4-nitrophenylazo)salicylaldehyde (9) (88 mg, 0.32 mmol/50 ml), and the resulting solution was heated under reflux for 20 hr. After left allowing to cool to room temperature, a precipitated solid was filtered and recrystallized from ethanol to give red crystals 4, mp 194 ~ 196°C (88 mg, 59% yield). Anal.: Found; C, 64.64; H, 4.76; N, 11.98%. Calcd. for C26H21N30Cl; C, 65.15; H, 4.59; N, 12.16%. MS: m/z (relative intensity); 462 (22), 461 (19), 460 (M+, 61), 195 (34), 194 (21), 193 (100), 192 (25), and 178 (12).1H NMR: δ ; 8.34 (distorted dt, J = 2.5, 8.6 Hz, 2H), 7.95 (distorted dt, J = 2.5, 8.6 Hz, 2H), 7.82 (dd, J = 2.2, 8.6 Hz, 1H), 7.74 (d, J = 2.3 Hz, 1H), 7.74 (dd, J = 2.0, 8.3 Hz, 1H), 7.04 (d, J = 2.3 Hz, 1H), 6.99
5',6-Dinitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (6): A two-phase mixture of a dichloromethane solution of 6-nitrobenzospiropyran 1 (242 mg, 0.752 mmol/10 ml) and sodium nitrite (53.9 mg, 0.781 mmol) in 2 mol dm$^{-3}$ aqueous sulfuric acid (20 ml) was agitated vigorously in the presence of sodium TFPB (36.5 mg, 0.0392 mmol) as a phase-transfer catalyst. After 10-hr reaction with agitation, the resulting green dichloromethane layer was washed with saturated aqueous sodium carbonate to afford a red solution, which turned again green when dried on anhydrous magnesium sulfate. The last solution was evaporated off and the residue was again dissolved in dichloromethane, reprecipitated by the addition of hexane. The mother liquor was chromatographed on a silica-gel column. Initially eluted fractions contained the starting material 1 (50 mg), and then subsequent ones a compound (78 mg) exhibiting a UV-band at 369 nm and the molecular peak at m/z = 367, which was identified to be 6 (28% yield), mp. 218-219°C (lit., mp. 177-178°C). UV(CH$_2$Cl$_2$): $\lambda_{max}$; 369 nm, $\varepsilon = 2.3 \times 10^4$. MS: m/z (rel. intensity); 368 (21), 367 (M$^+$, 100), 352 (28), 204 (62), 203 (12), 158 (13), and 49 (11). $^1$H-NMR: $\delta$; 8.20 (dd, $J=2.3$, 8.6 Hz, 1H), 8.06 (dd, $J=2.7$, 8.8 Hz, 1H), 8.04 (d, $J=2.6$ Hz, 1H), 7.96 (d, $J=2.3$ Hz, 1H), 7.00 (d, $J=10.3$ Hz, 1H), 6.80 (d, $J=8.8$ Hz, 1H), 6.55 (d, $J=8.6$ Hz, 1H), 5.85 (d, $J=10.3$ Hz, 1H), 2.87 (s, 3H), 1.35 (s, 3H), and 1.23 ppm (s, 3H). $^{13}$C-NMR: $\delta$; 158.8, 152.9, 141.5, 141.0, 136.9, 129.1, 126.3, 126.2, 122.9, 120.1, 118.3, 118.3, 115.6, 105.9, 105.7, 51.9, 28.9, 25.7, and 19.9 ppm.

5'-Chloro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (7): 5-Chloro-1,3,3-trimethyl-2-methyleneindoline (10) (4.20 g, 20.2 mmol) was added into an ethanol solution of salicylaldehyde (2.45 g, 20.1 mmol/200 ml), and the resulting solution was heated under reflux for 4 hr. The reaction mixture was evaporated off. The addition of methanol into the residue gave red-colored precipitate, which was washed with methanol to yield a colorless solid. Reprecipitation from a methanol solution by the addition of dichloromethane afforded a colorless solid 7, mp 154-155°C (lit. $^1$H-NMR: $\delta$; 7.11 (dd, $J=2.0$, 8.3 Hz, 1H), 7.09 (dt, $J=0.6$, 7.5 Hz, 1H), 7.04 (dd, $J=1.6$, 7.5 Hz, 1H), 7.01 (d, $J=2.0$ Hz, 1H), 6.85 (d, $J=10.3$ Hz, 1H), 6.82 (dt, $J=1.2$, 7.5 Hz, 1H), 6.70 (d, $J=7.5$ Hz, 1H), 6.41 (d, $J=8.3$ Hz, 1H), 5.64 (d, $J=10.3$ Hz, 1H), 2.70 (s, 3H), 1.28 (s, 3H), and 1.16 ppm (s, 3H). $^{13}$C-NMR: $\delta$; 154.2, 146.8, 138.7, 129.8, 129.7, 127.2, 126.7, 123.6, 122.0, 120.2, 118.7, 118.6, 114.9, 107.6, 104.2, 51.7, 28.9, 25.6, and 19.9 ppm.

5-(4-Nitrophenylazo)salicylaldehyde (9): Into an ethanolic buffer solution of salicylaldehyde (367 mg,
3.00 mmol) was added solid 4-nitrobenzenediazonium tetrafluoroborate (779 mg, 3.29 mmol), and stirred for a while. A solid precipitate was immediately formed, and was extracted with dichloromethane. Evaporation of the dichloromethane extracts, after washing in unusual manner, afforded solid residue, which was then washed with carbon tetrachloride and hexane, successively. The final solid residue (132 mg) was recrystallized from a methanol-dichloromethane mixture to yield crystals of 9, mp. 201°C (113 mg, 14% yield). Anal. Found; C, 57.30; H, 3.68; N, 15.28%. Calcd. for C_{13}H_{12}N_{3}O_{4}: C, 57.57; H, 3.34; N, 15.49%. MS: m/z (relative intensity); 272 (16), 271 (M⁺, 100), 149 (45), 122 (26), 121 (91), 93 (29), 76 (14), 75 (15), 65 (36), and 39 (19). ¹H-NMR: δ (CD₂Cl₂): 11.47 (s, 1H), 10.06 (s, 1H), 8.38 (dt, J=2.6, 8.8 Hz, 1H), 8.32 (dd, J=2.6, 8.8 Hz, 1H), 8.04 (dt, J=2.6, 8.8 Hz, 1H), and 7.16 ppm (d, J=9.2 Hz, 1H).

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References


(3) R. Ref. 1b), p. 72.


(7) Ref. 1b), p. 68.

(8) Ref. 1b), p. 62.

(9) Details are described in a) Ref. 1a), p. 418, and b) Ref. 1b), p. 253.


(11) The overlapped signal was splitted into two at 147.0 and 147.1 ppm upon measured in deuterodichloromethane.