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BISINDOLES. 42.* SYNTHESIS OF A NEW BISSPIROPYRAN SYSTEM DERIVED FROM INDOLO[4,5-*e*]INDOLE

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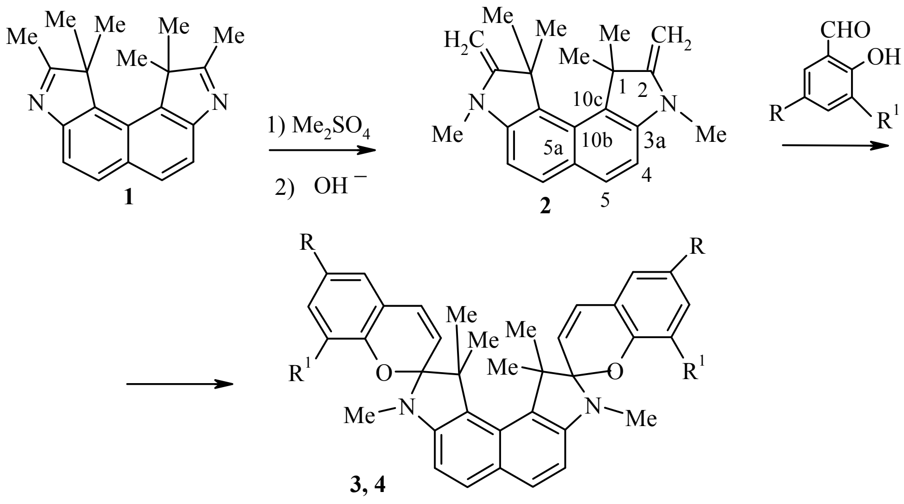
An active search is presently underway for bisspiro compounds with photochromic properties [2]. We have already synthesized bisspirocyclic dihydroindolizine systems from isomeric dihydroindolo[4,5-*e*]indoles and dihydroindolo[6,7-*g*]indoles [3, 4].

In the present work, we report the synthesis of a new condensed indoline bisspiropyran derived from hexamethyldihydroindoloindole **1**. The synthesis was carried out in three steps according to the following scheme:



3 R = NO_2, R^1 = H; **4** R = R^1 = Br

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* For Communication 41, see [1].

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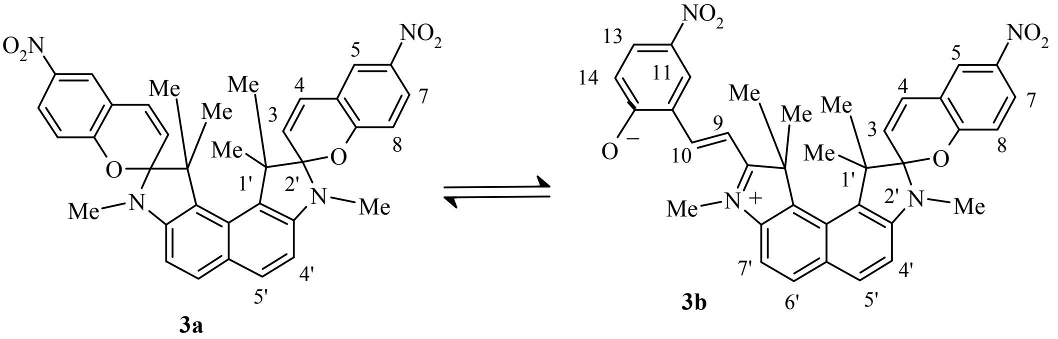
The quaternization of bisindolenine **1** by dimethyl sulfate gives the corresponding diquaternary salt, which is converted to the bisanalog of 2-methylindoline bases known as Fischer bases, namely, 1,1,3,8,10,10-hexamethyl-2,9-dimethylideneindolino[4,5-*e*]indoline (**2**) by treatment with warm 5% aqueous KOH. The third step of the synthesis involves condensation of the resultant bifunctional base **2** with a threefold excess of salicylaldehydes by heating in ethanol for 30-90 min at reflux. The desired products form colored crystals upon cooling of the reaction mixture. The new bisspiropyrans are 1',1',3',8',10',10'-hexamethyl-6,6"-dinitro- (**3**) and 6,6",8,8"-tetrabromo-1',1',3',8',10',10'-hexamethyldispiro[chromene-2,2'-indolino[4,5-*e*]indoline-9',2"-chromenes] (**4**).

The ^{1}H and ^{13}C NMR spectra of compound **2** show one set of signals which corresponds to the symmetrical structure of bifunctional molecule. Chemical shifts of equivalent protons and C atoms of each half of the molecule are identical and appear the signals of only one half.

The ^{1}H NMR spectra of products **3** and **4** show two sets of signals of different intensity. The high-intensity signals correspond to the symmetrical structure. The coupling constants of pyran protons H-3 and H-4 in *cis* arrangement ($J_{3,4}$ = 10 Hz) and chemical shift of the N(CH$_3$) group protons were used to assign these signals to closed bisspirocyclic structures **3a** and **4a**. The high-intensity signals of the protons of the pyran ring methyl groups were also assigned to the closed form since they are not equivalent and appear as two upfield singlets [6].

The low-intensity signals correspond to asymmetrical molecules of unilaterally opened bisspiro structures **3b** and **4b**, which were detected upon their dissolution in DMSO. The low-intensity signals show pyran proton doublets with coupling constants ~13-14 Hz, which is characteristic for *trans* arrangement of these protons in the open betaine structure of one half of the molecule.



The IR spectra were taken on UR-20 and Thermo Nicolet Avatar 370 FTIR spectrometers for vaseline mulls. The UV spectra were taken on a Varian Carry 100 UV-vis spectrometer. The ^{1}H and ^{13}C NMR spectra were taken on a Bruker AM-400 spectrometer at 400 and 100 MHz, respectively, in DMSO-d$_6$ with TMS as the internal standard. The mass spectra were taken on a Finnegan MAT 95 mass spectrometer manufactured in the United States.

1,1,3,8,10,10-Hexamethyl-2,9-dimethylideneindolino[4,5-*e*]indoline (2). Freshly-distilled dimethyl sulfate (12 ml) was added to hexamethyldihydroindolo[4,5-*e*]indole **1** (0.9 g, 2.8 mmol) [3] and heated at 100-110°C for 70 min. The reaction mixture was diluted by adding absolute ether. The tarry crude product was separated and washed with absolute ether. The resultant bisquaternary salt **2** was dissolved in a minimal amount of ethanol and warm 5% aqueous KOH was added. The precipitate was filtered off, washed with water, and dried to give 0.6 g (60%) compound **2** as a light-brown powder, mp 173-174°C, R_f 0.4 (Silufol UV-254, 20:1 ethanol–ammonia). IR spectrum, ν, cm^{-1}: 1643 (>C=CH$_2$). UV spectrum in ethanol, λ_{max}, nm (log ε): 218 (3.306), 246 (3.418), 259

(3.396), 312 (4.20), 380 (1.017), 541 (0.171). ^{1}H NMR spectrum (data for half of the molecule are given), δ, ppm (*J*, Hz): 1.62 (6H, s, C(CH_3)$_2$); 3.08 (3H, s, N–CH_3); 3.79 (2H, s, >C=CH_2); 6.94 (1H, d, J_o = 8.6, H Ar); 7.68 (1H, d, J_o = 8.6, H Ar). ^{13}C NMR spectrum, δ, ppm 28.93 (N–CH_3), 30.21 ((CH_3)$_2$), 47.04 (C-1), 72.35 (=CH_2), 105.74 (C-4), 122.00 (C-10*c*), 126.83 (C-5*a*), 129.66 (C-10*b*), 133.14 (C-5), 146.79 (C-3*a*), 165.98 (C-2). High-resolution electron impact mass spectrum, found: *m/z* 318.2079 [M]$^+$. $C_{22}H_{26}N_2$. Calculated M = 318.

1',1',3',8',10',10'-Hexamethyl-6,6"-dinitrodispiro[chromene-2,2'-indolino[4,5-*e*]indoline-9',2"-chromene] (3). Compound **2** (0.13 g, 0.41 mmol) was dissolved in ethanol, added to an ethanolic solution of 5-nitrosalicylaldehyde (0.17 g, 1 mmol), and heated at reflux for 30 min. The reaction mixture was left overnight. The precipitate formed was filtered off, washed with ethanol, and dried to give 100 mg (40%) compound **3**, R_f 0.6 (ethanol). IR spectrum, ν, cm^{-1}: 1654, 1607 (C=C pyran), 1530-1490 (NO_2 asym.), 1325 (NO_2 sym.), 1275 (N–C spiro), 1095, 945 (O–C spiro). UV spectrum in ethanol, λ_{max}, nm (log ε): 200 (0.500), 225 (0.630), 273 (0.611), 318.07 (0.412), 347 (0.428), 534 (0.238). ^{1}H NMR spectrum (data given for half of the molecule of the symmetrical closed form **3a**, high-intensity signals), δ, ppm (*J*, Hz): 1.47 (3H, s, 1'-CH_3); 1.61 (3H, s, 1'-CH_3); 2.78 (3H, s, N–CH_3); 6.13 (1H, d, $J_{3,4}$ = 10.5, H-3); 6.96 (1H, d, $J_{4',5'}$ = 8.4, H-4'); 7.31 (1H, d, $J_{3,4}$ = 10.5, H-4); 7.86 (1H, d, $J_{7,8}$ = 7.7, H-8); 8.17 (1H, d, $J_{4',5'}$ = H-5'); 8.22 (1H, dd, $J_{7,8}$ = 7.7, $J_{5,7}$ = 2.7, H-7); 8.37 (1H, d, $J_{5,7}$ = 2.7, H-5). ^{1}H NMR spectrum for the asymmetrical unilaterally opened form **3b** (low-intensity signals), δ, ppm (*J*, Hz): 1.87 (3H, s, 1'-CH_3); 1.88 (3H, s, 1'-CH_3); 2.13 (6H, s, 10'-CH_3); 2.92 (3H, s, N–CH_3); 3.94 (3H, s, N^+–CH_3); 6.15 (1H, d, $J_{3,4}$ = 10.3, H-3); 6.29 (1H, d, $J_{4',5'}$ = 9.6, H-4'); 6.83 (1H, d, $J_{6',7'}$ = 9.1, H-6'); 6.89 (1H, d, $J_{4',5'}$ = 9.6, H-5'); 7.34 (1H, d, $J_{6',7'}$ = 9.1, H-7'); 7.41 (1H, d, $J_{3,4}$ = 10.3, H-4); 7.73 (1H, d, $J_{7,8}$ = 8.9, H-8); 7.96 (1H, dd, $J_{7,8}$ = 8.9, $J_{5,7}$ = 2.4, H-7); 8.04 (1H, d, $J_{13,14}$ = 8.9, H-14); 8.13 (1H, dd, $J_{13,14}$ = 8.9, $J_{11,13}$ = 2.4, H-13); 8.14 (1H, d, $J_{9,10}$ = 13.3, H-9); 8.25 (1H, d, $J_{9,10}$ = 13.3, H-10); 8.31 (1H, d, $J_{5,7}$ = 2.4, 5-H); 8.62 (1H, d, $J_{11,13}$ = 2.4, H-11). Found, %: C 69.82; H 4.78; N 9.05. $C_{36}H_{32}N_4O_6$. Calculated, %: C 70.12; H 5.23; N 9.09.

6,6",8,8"-Tetrabromo-1',1',3',8',10',10'-hexamethyldispiro[chromene-2,2'-indolino[4,5-e]indoline-9',2"-chromene] (4) was obtained from compound **2** (0.19 g, 0.6 mmol) and 3,5-dibromosalicylaldehyde (0.33 g, 1.2 mmol) upon heating at 40°C for 1 h. The yield of compound **4** was 28% (140 mg). R_f 0.8 (ethanol). IR spectrum, ν, cm^{-1}: 1610 (C=C pyran), 1550 (C=C conj. pyran), 1280 (N–C spiro), 1080, 900 (O–C spiro). UV spectrum in ethanol, λ_{max}, nm (log ε): 199 (0.576), 231 (0.71), 273 (0.584), 576 (0.174). ^{1}H NMR spectrum (data are given for half of the molecule of the symmetrical closed form **4a**, high-intensity signals), δ, ppm (*J*, Hz): 1.44 (3H, s, 1'-CH_3); 1.61 (3H, s, 1'-CH_3); 2.74 (3H, s, N–CH_3); 6.04 (1H, d, $J_{3,4}$ = 10.3, H-3); 6.93 (1H, d, $J_{4',5'}$ = 8.5, H-4'); 7.11 (1H, d, $J_{3,4}$ = 10.3, H-4); 7.47 (1H, d, $J_{5,7}$ = 2.2, H-7); 7.54 (1H, d, $J_{5,7}$ = 2.2, H-5); 7.82 (1H, d, $J_{4',5'}$ = 8.5, H-5'). ^{1}H NMR spectrum of the asymmetrical unilaterally open form compound **4b** (low-intensity signals), δ, ppm, (*J*, Hz): 1.82 (3H, s, 1'-CH_3); 1.87 (3H, s, 1'-CH_3); 2.07 (6H, s, 10'-CH_3); 2.89 (3H, s, N–CH_3); 3.88 (3H, s, N^+–CH_3); 5.96 (1H, d, $J_{3,4}$ = 10.3, H-3); 6.90 (1H, d, $J_{6',7'}$ = 8.5, H-6'); 7.06 (1H, d, $J_{3,4}$ = 10.3, H-4); 7.30 (1H, d, $J_{4',5'}$ = 8.8, H-5'); 7.55 (1H, d, $J_{11,13}$ = 2.4, H-13); 7.57 (1H, d, $J_{5,7}$ = 2.4, H-7); 7.62 (1H, d, $J_{5,7}$ = 2.5, H-5); 7.64 (1H, d, $J_{4',5'}$ = 8.8, H-4'); 7.65 (1H, d, $J_{11,13}$ = 2.4, H-11); 7.75 (1H, d, $J_{6',7'}$ = 8.5, H-7'); 8.10 (1H, d, $J_{9,10}$ = 13.3, H-9); 8.11 (1H, d, $J_{9,10}$ = 13.3, H-10). High-resolution electron impact mass spectrum (70 eV), found, *m/z*: 838.9108, 840.9407, 841.9230, 843.9518, 844.9273 [M]$^+$. $C_{36}H_{30}Br_4N_2O_2$. Calculated M: 842. Spirochromenes **3** and **4** do not melt below 350°C.

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