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DIPYRROLOQUINOXALINES. 1. SYNTHESIS OF A NEW BISSPIROPYRAN SYSTEM DERIVED FROM BENZO[*e*]PYRROLO[3,2-*g*]INDOLE

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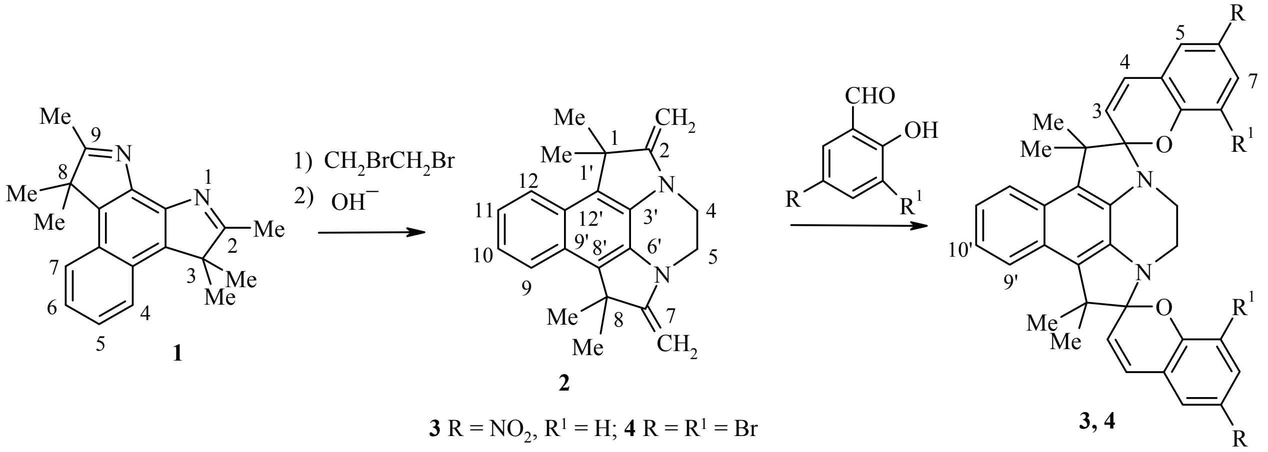
In previous work [1], we reported the synthesis of spirocyclic dihydroindolizine systems derived from 2,3,3,8,9,9-hexamethyl-3,8-dihydrobenzo[*e*]pyrrolo[3,2-*g*]indole (**1**). In a continuation of work on the synthesis of bisspiro compounds, we report the synthesis of a new bisspiro system, namely, 1',1',8',8'-tetramethyl-1',4',5',8'-tetrahydrospiro[chromene-2,2'-dipyrrolo[1,2,3-*d*,*e*:3,2,1-*i*,*j*]benzo[*g*]quinoxaline-7',2''-chromene].

The alkylation of hexamethyldihydrobenzo[*e*]pyrrolo[3,2-*g*]indole **1** by dibromoethane gives a biquaternary salt, which was converted by treatment with 5% aqueous KOH into the bisanalog of 2-methylene-indoline bases known as Fischer bases, namely, 1,1,8,8-tetramethyl-2,7-dimethylidene-1,2,4,5,7,8-hexahydrodipyrrolo[1,2,3-*d,e*:3,2,1-*i,j*]benzo[*g*]quinoxaline (**2**). 2-Methylideneindoline bases are important intermediates in the synthesis of a variety of organic compounds [2].



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

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The condensation of compound **2** was carried out by warming with a threefold excess of 5-nitro- and 3,5-dibromosalicylaldehydes in ethanol at 30-40°C for 30-45 min. After cooling, a colored crystalline precipitate was obtained. Derivatives of a new bisspiropyran system were obtained: 1',1',8',8'-tetramethyl-6,6"-dinitro-1',4',5',8'-tetrahydroidispiro[chromene-2,2'-dipyrrolo[1,2,3-*d,e*:3,2,1-*i,j*]benzo[*g*]quinoxaline-7',2"-chromene] (**3**) and 6,6",8,8"-tetrabromo-1',1',8',8'-tetramethyl-1',4',5',8'-tetrahydrodispiro[chromene-2,2'-dipyrrolo[1,2,3-d,e:3,2,1-i,j]-benzo[g]quinoxaline-7',2"-chromene] (4).

The NMR spectra of compounds **3** and **4** show a single set of signals, which corresponds to a symmetrical structure of the bifunctional molecule. The chemical shifts of equivalent protons and carbon atoms of each half of the molecule are identical and signals appear only for one half of the molecule.

The chemical shifts of the protons of the two *gem*-methyl groups in the ^{1}H NMR spectrum of compound **2** coincide and appear as a singlet with integral intensity of 12H. The chemical shifts of the quinoxaline ring CH_2 groups are also identical (4H, s). The signals of the protons of the exocyclic $>C=CH_2$ group appear as a doublet. The aromatic protons are seen as doublets with *ortho* coupling constants.

The ^{13}C NMR spectrum of compound **2** has signals characteristic for the carbon atoms of 2-methylideneindolines [2]: C(1) (67.19), C(2) (166.53), and the exocyclic methylene atom (77.86 ppm). The signals for the carbon atoms in the N–CH_2 and *gem*-methyl groups are seen at 49.27 and 28.88 ppm, respectively. The spectrum also shows signals for the aromatic carbon atoms.

The doublets for pyran protons H-3 and H-4 in the ^{1}H NMR spectrum of bisspiro compounds **3** and **4** have coupling constants indicating their *cis* arrangement ($J_{3,4}$ = 10.0 Hz). The signals for the protons of the N–CH_2–CH_2–N groups are also doublets and their chemical shifts correspond to the closed bisspirocyclic structure. The high-intensity signals of the protons of the geminal methyl groups in the pyrrolidine ring are also assigned to the closed form since, in this case, they are not equivalent and appear as two upfield singlets [3].

The IR spectra were taken on UR-20 and Thermo Nicolet Avatar 370 FT-IR spectrometers for vaseline mulls (**2** and **3**) and in KBr pellets (**4**). 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 a 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.

1,1,8,8-Tetramethyl-2,7-dimethylidene-1,2,4,5,7,8-hexahydropyrrolo[1,2,3-*d,e*:3,2,1-*i,j*]benzo[*g*]quinoxaline (2). A mixture of benzopyrroloindole **1** (0.3 g, 0.1 mmol) and 1,2-dibromoethane (5 ml) was heated in a sealed ampule for 8 h at 160°C. The melt was washed with ether and acetone to give a brown powder of compound **1** dibromide in a quantitave yield. The residue (0.35 g) was dissolved in boiling water and filtered. The filtrate was brought to pH 10 by adding warm 5% aqueous KOH. The precipitate of **2** was filtered off, washed with water until the wash water was neutral, and dried to give 0.072 g (39%) **2** as a cream-colored powder, R_f 0.6 (20:1 ethanol–ammonia). This product decomposes at 230°C. IR spectrum, ν, cm^{-1}: 1635 ($>C=CH_2$). UV spectrum in benzene, λ_{max}, nm (log ε): 270 (1.244), 287 (3.583), 368 (1.516), 381 (1.573). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.58 (12H, s, $C(CH_3)_2$); 3.64 (4H, s, –N–CH_2–CH_2–N–); 4.18, 4.10 (4H, 2d, *J* = 1.9, $>C=CH_2$); 7.13, 7.50 (4H, 2dd, J_o = 6.4, J_m = 3.5, H Ar). ^{13}C NMR spectrum, δ, ppm: 28.88 (CH_3), 49.27 (–N–CH_2–CH_2–N–), 67.19 (C-1, C-8), 77.86 (=CH_2), 116.22 (C-1', C-8'), 121.85 (C-9, C-12), 122.74 (C-10, C-11), 126.86 (C-9', C-12'), 130.30 (C-3', C-6'), 166.53 (C-2, C-7). High-resolution electron impact mass spectrum (70 eV), found, *m/z*: 316.1933 $[M]^+$. $C_{22}H_{24}N_2$. Calculated, M = 316.

1',1',8',8'-Tetramethyl-6,6"-dinitro-1',4',5',8'-tetrahydrodispiro[chromene-2,2'-dipyrrolo[1,2,3-*d,e*:3,2,1-*i,j*]benzo[*g*]quinoxaline-7',2"-chromene] (3). Compound **2** (50 mg, 0.16 mmol) was dissolved in absolute ethanol (7 ml) and an ethanolic solution 5-nitrosalicylaldehyde (75 mg, 0.45 mmol) was added. The mixture was stirred for 10 min in the dark at 40°C. After cooling of the dark-violet solution, 0.03 g (30%) compound **3** was filtered off as a dark-blue powder, mp 158°C, R_f 0.6 (benzene). IR spectrum, ν, cm^{-1}: 1644-1615 (C=C pyran), 1526 (NO_2 asym.), 1342 (NO_2 sym), 1269 (N–C spiro), 1169-1122, 963, 906, 816 (O–C spiro). UV spectrum in ethanol, λ_{max}, nm (log ε): 225 (1.867), 269 (2.554), 315 (0.964), 558 (0.121). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.43 (6H, s, $C(CH_3)_2$); 1.62 (6H, s, $C(CH_3)_2$); 3.19 (2H, d, J_{CH2CH2} = 7.3, –CH$_2$–N–); 3.29 (2H, d, J_{CH2CH2} = 7.3, –CH$_2$–N–); 5.94 (2H, d, $J_{3,4}$ = 10.1, H-3); 6.79 (2H, d, $J_{7,8}$ = 8.5, H-8); 6.92 (2H, d, $J_{3',4'}$ = 10.1, H-4); 7.25 (2H, dd, $J_{9',10'}$ = 6.4, $J_{10',12'}$ = 3.5, H-10'); 7.85 (2H, dd, $J_{9',10'}$ = 6.4, $J_{9',11'}$ = 3.5, H-9'); 8.01 (2H, dd, $J_{7,8}$ = 8.5, $J_{5,7}$ = 2.5, H-7); 8.02 (2H, d, $J_{5,7}$ = 2.5, H-5). Found, %: C 70.01; H 5.7; N 8.82. $C_{36}H_{30}N_4O_6$. Calculated, %: C 70.35; H 4.92; N9.12.

6,6",8,8"-Tetrabromo-1',1',8',8'-tetramethyl-1,'4,'5,8'-tetrahydrodispiro[chromene-2,2'-dipyrrolo-[1,2,3-*d,e*:3,2,1-*i,j*]benzo[*g*]quinoxaline-7',2"-chromene] (4) was obtained as a green powder analogously to **3** from compound **2** (60 mg, 0.19 mmol) and 3,5-dibromosalicylaldehyde (80 mg, 0.45 mmol) upon heating at 45°C for 45 min. The yield of compound **4** was 0.08 g (50%), R_f 0.8 (1:1 benzene–hexane), mp 238-240°C. IR spectrum, ν, cm^{-1}: 1643 (C=C pyran), 1535, 1442 (C=C, conj. pyran), 1265 (N–C spiro), 1157, 964, 887 (O–C spiro). UV spectrum in chloroform, λ_{max}, nm (log ε): 246 (3.731), 273 (0.420), 319 (1.081), 359 (0.759), 620 (0.17). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.36 (6H, s, $C(CH_3)_2$); 1.55 (6H, s, $C(CH_3)_2$); 3.05 (2H, d, J_{CH2CH2} = 7.2, N–CH$_2$–); 3.20 (2H, d, J_{CH2CH2} = 7.2, CH$_2$–N–); 6.06 (2H, d, $J_{4,3}$ = 10.0, H-3); 7.05 (2H, d, $J_{3,4}$ = 10.4, H-4); 7.20-7.22 (2H, m, H-10'); 7.52 (2H, s, H-7), 7.61 (2H, s, H-5), 7.82-7.85 (2H, m, H-9'). High-resolution mass impact mass spectrum (70 eV), found: *m/z* 837.9262, 839.9397, 841.9388 [M]$^+$. $C_{36}H_{28}Br_2N_2O_2$. Calculated, M = 840.

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