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LETTERS TO THE EDITOR

PYRROLOINDOLES. SYNTHESIS OF NEW SPIROCYCLIC SYSTEMS DERIVED FROM BENZO[*e*]PYRROLO[3,2-*g*]INDOLE

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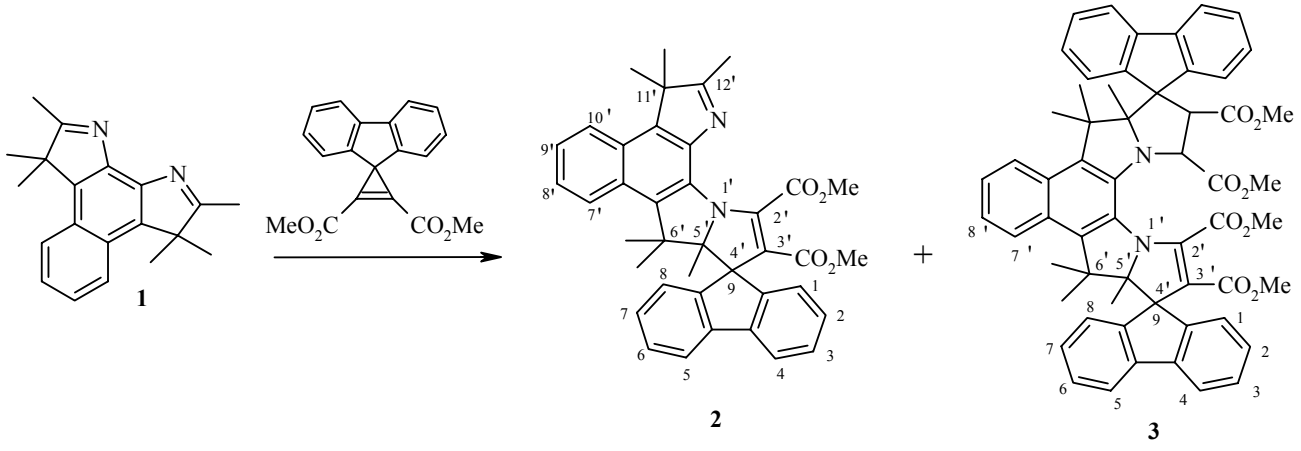
Spirocyclic dihydroindolizine systems from isomeric indolenino[4,5-*e*]- and indolenino[6,7-*g*]indolenines synthesized in our previous work[1, 2] proved to be rapidly converting photochromic systems with very short periods for 50% conversion of the colored form [3].

A synthesis of new spirocyclic systems was carried out using the reaction of 2',3'-dimethoxycarbonylspirofluorenecyclopropene with 2,3,3,8,9,9-hexamethyl-3,8-dihydrobenzo[*e*]pyrrolo[3,2-*g*]indole (**1**) [4]. The main reaction product was a monospiro compound, namely, 2',3'-dimethoxycarbonyl-5',6',6',11',11',12'-hexamethyl-11'-hydrospirofluorene-9,4'-(1'-aza-2'-cyclopentene)[1',5'-*a*]benzo[*e*]pyrrolo[3,2-*g*]indoline (**2**) obtained in 71% yield. A bis-spirocyclic system, bis(2',3'-dimethoxycarbonyl-5',6',6'-trimethylspirofluorene-9,4'-(1'-aza-2'-cyclopentene)[1',5'-*a*]benzo[*e*]pyrrolino[3,2-*g*]indoline (**3**), was formed in 5% yield. This yield was not improved by raising the temperature or increasing the time of the reaction, probably due to steric factors.



1 **2** **3**

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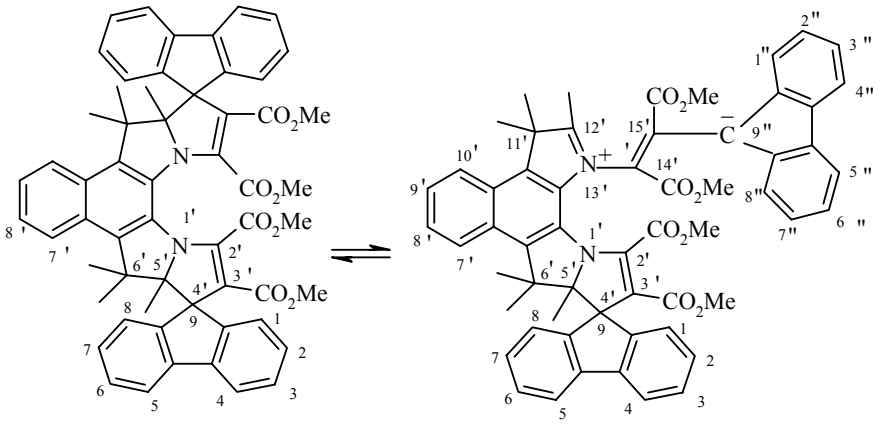
The structures of **2** and **3** were demonstrated using IR, UV, and ^{1}H NMR spectroscopy and mass spectrometry. The chemical shifts of the two CH_3 groups at C-11' in the ^{1}H NMR spectrum of **2** coincide and appear as a singlet at δ 1.27 ppm, corresponding in integral intensity to six protons. The chemical shifts of fluorene protons, δ(H-1) = δ(H-8) and δ(H-4) = δ(H-5), also coincide and their signals appear as doublets. The signals of H-7' and H-10' protons are doublets; only four doublets appear, which correspond to six protons. The chemical shifts of the following triplets coincide analogously: δ(H-3) = δ(H-6) = 7.35 and δ(H-2) = δ(H-7) = 7.47 ppm. The signals of H-8' and H-9' protons are also triplets; four triplets are obtained corresponding to six protons.



3a **3b**

The ^{1}H NMR spectrum of **3** shows two sets of signals of different intensity. The strong-intensity signals correspond to a symmetrical structure of the closed form of bis-spiro compound **3a**, while the low-intensity signals correspond to an asymmetrical, unilaterally-opened spiro compound **3b**, which was detected upon dissolving **3** in DMSO. We should note that the low-intensity signals in the spectrum of **3** in the range 6.01-6.94 ppm were assigned to protons of the fluorene fragment in the open half of structure **3b**, while the signals at 7.04-8.07 ppm correspond to the protons of the fluorene fragment of the closed half of the spiro compound and the naphthalenic part of structure **3b**.

The reaction course, monitoring of the purity of the products, and determination of the R_f values were carried out on Silufol UV-254 plates. Silica gel with particle size 100-250 μm was used as the adsorbent in column chromatography. The IR spectra were taken on a Termo Nikolet Avatar-370 spectrometer equipped with FTIR in vaseline mull. The UV spectra were taken on a Varian Carry 100 UV-Vis spectrometer. The ^{1}H NMR spectra were taken on a Bruker DRX-500 spectrometer at 500 MHz with TMS as the internal standard. The error of the chemical shift measurement was δ±0.01 ppm and the error for the coupling constant was ±0.1 Hz. The mass spectra were taken on a Finnegan MAT 95 CI (chemical ionization) mass spectrometer.

2',3-Dimethoxycarbonyl-5,6',6'11',11',12'-hexamethyl-11'-hydrospirofluorene-9,4'-(1'-aza-2'-cyclopentene)[1',5'-*a*]benzo[*e*]pyrrolo[3,2-*g*]indoline (2). A solution of benzopyrroloindole **1** (0.08 g, 0.28 mmol) in 3 ml absolute benzene was added to a solution of 2',3'-dimethoxycarbonylspirofluorenecyclopropene (0.25 g, 0.7 mmol) in absolute benzene (3 ml) and stirred in the dark for 5 h at 60°C. Evaporation of the benzene gave an oily product, which was converted to a precipitate using benzene–hexane. The precipitate was filtered off. Chromatography gave 0.14 g chromatographically-pure compound **2**. An additional compound **2** (0.12 g) and compound **3** (0.01 g, 5%) were obtained by column chromatography of the filtrate. The total yield of compound **2** was 71%; mp 143°C, R_f 0.4 (benzene). IR spectrum, ν, cm^{-1}: 1850, 1720, 1600, 1270, 1060, 815, 740. UV spectrum ($CHCl_3$), λ_{max}, nm (log ε): 378 (0.16), 269 (1.94), 240 (1.84), 202 (0.72). UV spectrum (after irradiation of the solution with light of mercury lamp), λ_{max}, nm (log ε): 260 (3.337), 210 (0.980). ^{1}H NMR

spectrum, δ, ppm (*J*, Hz): 0.90 (3H, s, 6'-CH_3); 1.12 (3H, s, 6'-CH_3); 1.27 (6H, s, 11'-CH_3); 1.67 (3H, s, 5'-CH_3); 1.81 (3H, s, 12'-CH_3); 3.34 (3H, s, CO_2CH_3); 3.78 (3H, s, CO_2CH_3); 7.28 (2H, d, ^3J = 9.4, H-1, H-8); 7.35 (2H, t, ^3J = 9.4, ^3J = 8.6, H-2, H-7); 7.40 (1H, t, ^3J = 9.9, ^3J = 8.6, H-8'); 7.47 (2H, t, ^3J = 9.4, ^3J = 8.6, H-3, H-6); 7.54 (1H, d, ^3J = 8.6, H-7'); 7.76 (1H, t, ^3J = 8.6, ^3J = 9.9, H-9'); 7.80 (1H, d, ^3J = 8.6, H-10'); 7.98 (2H, d, ^3J = 9.4, H-4, H-5). Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 596 $[M]^+$ (1.6), 537 (1.6), 478 (0.2), 418 (3.2), 403 (1.2), 306 (6.5), 274 (100), 262 (1.6), 247 (28), 220 (11.4), 203 (13.1), 189 (33.6), 78 (50.0). Found, %: C 78.42; H 6.10; N 4.74. $C_{30}H_{36}N_2O_4$. Calculated, %: C 78.52; H 6.04; N 4.70. M 596.

Bis(2',3'-dimethoxycarbonyl-5',6',6'-trimethylspirofluorene-9,4'-(1'-aza-2'-cyclopentene)[1',5'-*a*]-benzo[*e*]pyrrolino[3,2-*g*]indoline (3) was separated from the filtrate in the preparation of compound **2** (see previous synthesis) by column chromatography on silica gel with benzene as the eluent. The yield of compound **3** was 5%; mp 203°C, R_f 0.19 (benzene). IR spectrum, ν, cm^{-1}: 1720, 1710, 1590, 1570, 1270-1200, 1120, 1060, 760, 740. UV spectrum (benzene), λ_{max}, nm (log ε): 355 (0.78), 281 (3.85). UV spectrum (after irradiation of the solution with light of mercury lamp), λ_{max}, nm (log ε): 2.82 (4.03). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) (data for half of the molecule of symmetrical closed form of compound **3a**, high-intensity signals): 1.50 (3H, s, 6'-CH_3); 1.55 (3H, s, 6'-CH_3); 2.335 (3H, s, 5'-CH_3); 3.22 (3H, s, CO_2CH_3); 3.94 (3H, s, CO_2CH_3); 7.61 (2H, d, ^3J = 7.0, H-4, H-5); 7.80 (2H, d, ^3J = 8.0, H-1, H-8); 7.82 (2H, t, ^3J = 8.0, ^3J = 7.0, H-2, H-7); 7.39 (2H, t, ^3J = 7.0, ^3J = 7.0, H-3, H-6); 7.55 (1H, t, ^3J = 8.0, ^3J = 7.5, H-8'); 7.71 (1H, d, ^3J = 7.5, H-7'). The ^{1}H NMR spectrum for the asymmetrical unilaterally-open form **3b**, low-intensity signals: 1.13 (3H, s, CH_3); 1.15 (3H, s, CH_3); 1.23 (3H, s, CH_3); 1.25 (3H, s, CH_3); 2.01 (3H, s, CH_3); 2.02 (3H, s, CH_3); 3.09 (3H, s, CO_2CH_3); 3.52 (3H, s, CO_2CH_3); 3.75 (3H, s, CO_2CH_3); 3.83 (3H, s, CO_2CH_3); 6.01 (2H, d, ^3J = 8.0, H-1", H-8"); 6.34 (2H, t, ^3J = 8.0, ^3J = 7.9, H-2", H-7"); 6.69 (2H, d, ^3J = 7.0, H-4", H-5"); 6.94 (2H, t, ^3J = 8.0, ^3J = 7.0, H-3", H-6"); 7.04 (2H, t, ^3J = 7.5, ^3J = 7.5, H-3, H-6); 7.27 (1H, t, ^3J = 9.0, H-9'); 7.32 (1H, t, ^3J = 9.0, H-8'); 7.34 (1H, d, ^3J = 9.0, H-7'); 7.35 (1H, d, ^3J = 9.0, H-10'); 7.49 (2H, d, ^3J = 7.5, H-4, H-5); 7.73 (2H, t, ^3J = 8.0, ^3J = 7.5, H-2, H-7); 8.07 (2H, d, ^3J = 7.5, H-1, H-8). Mass spectrum (70 eV), *m/z* (I_{rel}, %): 902 $[M]^+$ (1.7), 747 (0.8), 735 (0.8), 627 (20), 598 (21.6), 582 (10.4), 566 (8.8), 535 (19.2), 446 (24), 388 (24.0), 377 (25.6), 326 (31.2), 308 (33.6), 292 (38.4), 263 (56), 252 (33.6), 248 (40.8), 205 (78), 193 (64.6), 189 (61.6), 165 (100). Found, %: C 78.23; H 5.62; N 3.15. $C_{58}H_{50}N_2O_8$. Calculated, %: C 77.16; H 5.54; N 3.10. M 902.

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