Formation of the fused system 5*H*,7*H*-pyrido[2,3-*b*:6,5-*b*´]diindole from 3-arylidene-2-ethoxyindolenines and hydrazine hydrate

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Three 12-aryl-5*H*,7*H*-pyrido[2,3-*b*:6,5-*b*´]diindoles (Ar = Ph, 4-BrC_6H_4, and 4-MeOC_6H_4) were obtained from appropriate 3-arylidene-2-ethoxyindolenines and hydrazine hydrate.

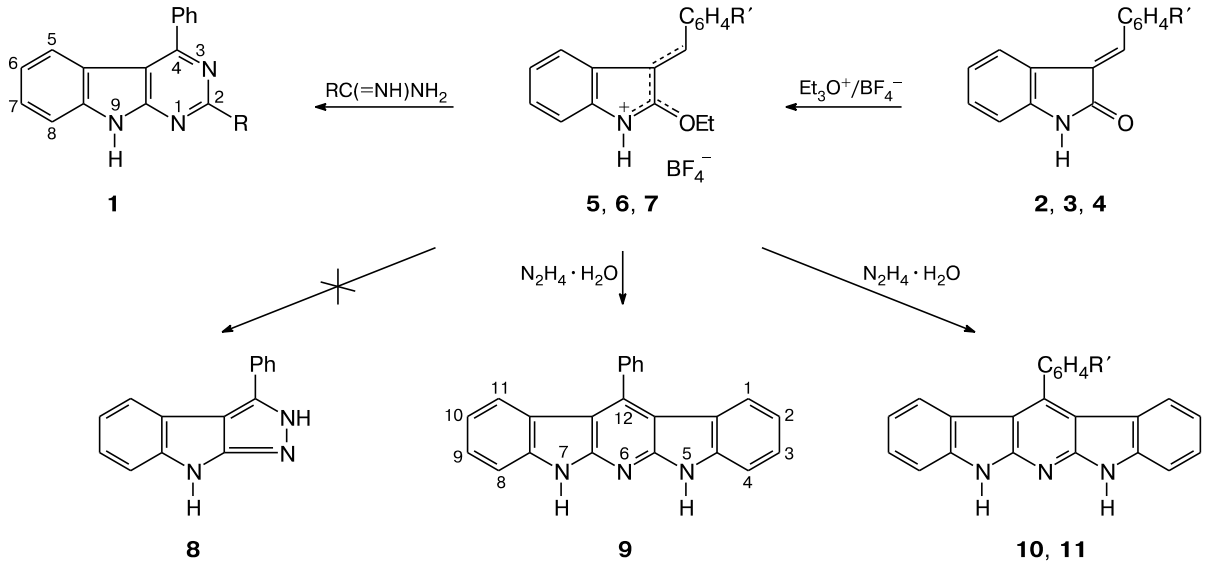
Key words: 3-arylidene-2-ethoxyindoleninium tetrafluoroborates, 12-aryl-5*H*,7*H*-pyrido-[2,3-*b*:6,5-*b*´]diindoles, cyclocondensation.

Earlier, we have proposed a route to a number of 2-substituted 4-aryl-9*H*-pyrimido[4,5-*b*]indoles **1** *via* reactions of 3-arylideneindolin-2-ones **2**—**4** (preconverted into reactive lactim ether forms) with such binucleophiles as amidines, guanidine, nitroguanidine, and alkylisothioureas[1—4] (Scheme 1). The next step in this direction was the synthesis of other fused heterocyclic systems from preparatively accessible indolin-2-ones. For this purpose, we studied reactions of hydrazine hydrate with a lactim ether generated from 3-benzylidene-2-ethoxyindoleninium tetrafluoroborate (**5**). It has been reported[5,6] that hydrazine hydrate reacts with carbocyclic and heterocyclic lactams to give heterocyclic systems of five fused rings, provided that the starting lactams containing a cyano or ester group in the α-position relative to the carbonyl group are first transformed into reactive lactim ethers. These data suggested that an analogous reaction of compound **5** with hydrazine hydrate could result in the formation of the pyrazole ring annulated to the indole one, thus yielding 3-phenylpyrazolo[3,4-*b*]indole (**8**).

However, this reaction did not lead to the expected product **8**. Instead, we obtained a compound in 23% yield, its molecular weight corresponding to the empirical formula $C_{23}H_{15}N_3$ (HRMS data).

We examined the ^1H and ^{13}C NMR spectra of this compound using 2D experiments (COSY, HSQC, and

Scheme 1



R = Me, Ph, NH_2, $NHNO_2$, $NHSO_2Ar$, SMe, SEt (**1**); R´ = H (**2**, **5**), 4-Br (**3**, **6**, **10**), 4-MeO (**4**, **7**, **11**)

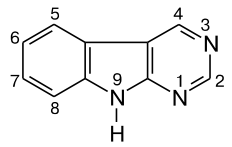
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 324—329, February, 2012.

COLOC). The ^{1}H NMR spectrum shows a low-field singlet for two NH groups, a complex multiplet for one phenyl group, and four multiplets of double intensity at δ 6.90—7.80 characteristic of indoles having no substituents in the benzene ring. This spectral pattern suggested the presence of two symmetrical indole moieties and a phenyl group in the structure of the compound obtained. So we formulated it as 12-phenyl-5*H*,7*H*-pyrido-[2,3-*b*:6,5-*b*´]diindole (**9**). The chemical shifts of the signals for the indole protons and carbon atoms mostly agree with the NMR data for substituted 9*H*-pyrimido[4,5-*b*]-indole[7] and 6*H*-indolo[2,3-*b*]quinoline.[8] However, the doublet we assigned to the H(1) and H(11) protons is substantially shifted upfield compared to the signal for the analogous H(5) proton in both the parent 9*H*-pyrimido-[4,5-*b*]indole and structurally related compound **1** (R = Me). This discrepancy can stem from the conformational features of compound **9**.

To refine its structure, we studied X-ray diffraction from the crystalline solvate $2C_{23}H_{15}N_3 \cdot CHCl_3$ grown from a chloroform solution (Fig. 1).

According to the data obtained, the unit cell of the crystal structure **9** consists of two crystallographically independent molecules. The pentacyclic framework is nearly planar (to within ±0.08 and ±0.09 Å), making an angle of 73.30(8)° and 83.57(8)° with the phenyl ring. When an external magnetic filed is applied to a sample of compound **9** during an NMR experiment, this field induces a ring current in the phenyl substituent that creates diamagnetic shielding around the aromatic H(1) and H(11) protons and causes their resonance signal to shift upfield. According to our calculations, the H(1) and H(11) protons are distant from the center of the benzene ring of the phenyl substituent at, on average, 3.02 Å for normalized C—H bond lengths. The GIAO—HF/6-31G*-calculated maps[9] of the anisotropic effect of the ring current in the phenyl substituent with allowance for the aforementioned geometrical parameters of structure **9** reveal that the anisotropic effect of the orthogonally oriented phenyl substituent on the nearest H(1) and H(11) protons should be 2—1 ppm when the resonating proton is distant from the plane of the benzene ring by 3—4 Å, respectively.[9]

The positions of the signals for the indole protons in the ^{1}H NMR spectrum of compound **9** as well as the positions of the signals for analogous protons in unsubstituted 9*H*-pyrimido[4,5-*b*]indole and its 2-methyl-4-phenyl derivative **1** (R = Me) are schematically shown in Fig. 2. The diamagnetic shift of the signal for the H(1) and H(11) protons in compound **9** compared to the signal for the H(5) proton in pyrimidoindole (**P**) is 1.2 ppm, which agrees with the theoretical prediction.



P

In compound **1**, the ring current of the phenyl group produces a weaker shielding effect on the indole protons (see Fig. 2) because the angle between the plane of this substituent and the heterocyclic framework does not exceed 42.7° (X-ray diffraction data[3]); in addition, the distance between the H(5) atom and the center of the benzene ring of the phenyl substituent increases to 3.40 Å.

In compound **9**, the aromatic protons H(2), H(10), H(3), H(9), and H(4), H(8) are farther away from the phenyl substituent and the diamagnetic shielding of these protons gradually becomes weaker, which is manifested in the positions of the signals for H(2) and H(10) in the ^{1}H NMR spectrum.

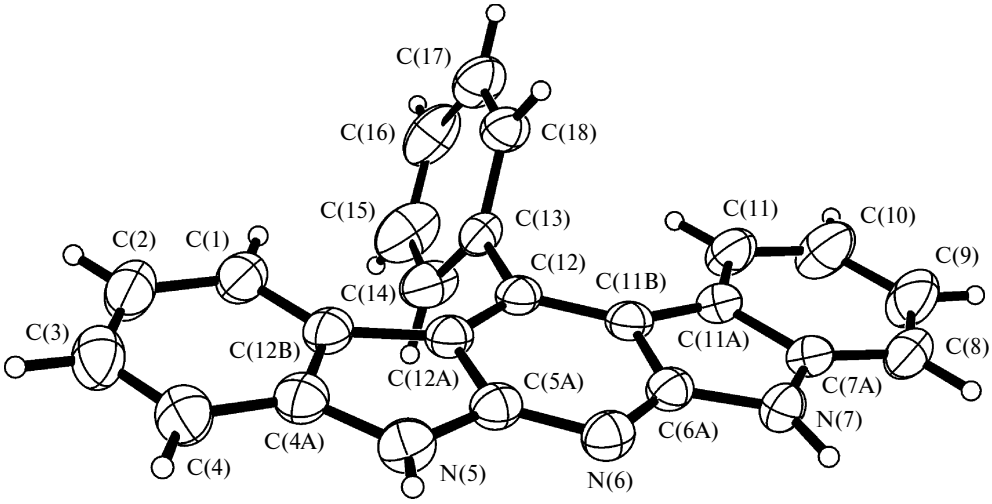


Fig. 1. One of two crystallographically independent molecules in structure **9** with atomic displacement ellipsoids (p = 50%).

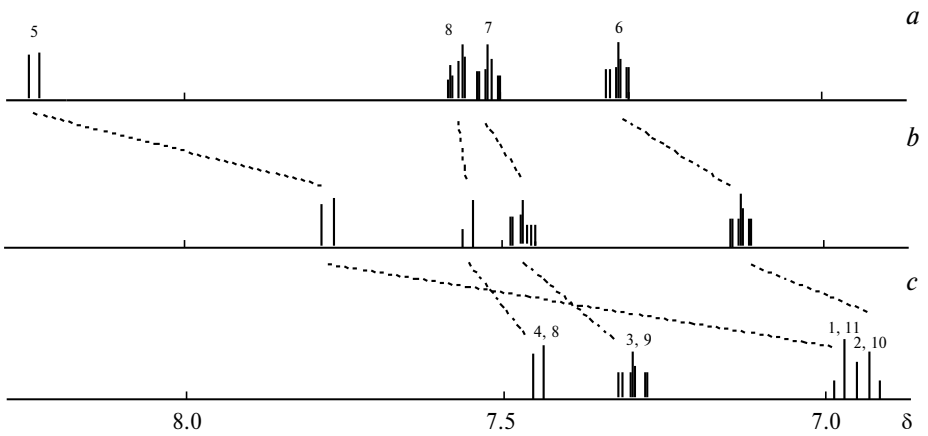


Fig. 2. Positions of the signals for the aromatic protons of the indole fragments in the ^{1}H NMR spectra (DMSO-d_6) of 9*H*-pyrimido[4,5-*b*]indole (**P**) (*a*), 2-methyl-4-phenyl-9*H*-pyrimido[4,5-*b*]indole **1** (*b*), and 12-phenyl-5*H*,7*H*-pyrido[2,3-*b*:6,5-*b*´]diindole (**9**) (*c*).

Earlier,[10—12] structurally related *N*(5),*N*(7)-dimethyl- and *N*(5),*N*(7)-dibenzylpyridodiindoles have been obtained by reactions of 2-amino-1-methyl- and 2-amino-1-benzylindoles with carbonyl compounds. The proposed[10—12] sequence of transformations leading to the annulated pyridine ring implies the formation of a bis(aminoindolyl)methylene intermediate containing two identical enamine moieties. At a final step, the amino group of one moiety attacks the α-C atom of the other enamine moiety to give, through elimination of an ammonia molecule and dehydrogenation, the pyridodiindole system. The ratio of the nucleophilicity of the amino group and the electrophilicity of the α-C atom of the enamine moieties is essential for the cyclization reaction. Attempts to increase the yield of the target product by using an oxindole derivative as a second condensation component (instead of aminoindole) in the final step of the reaction were unsuccessful. This provides clear evidence that the amide CO group of oxindole is inert to N-nucleophiles in these transformations.[11]

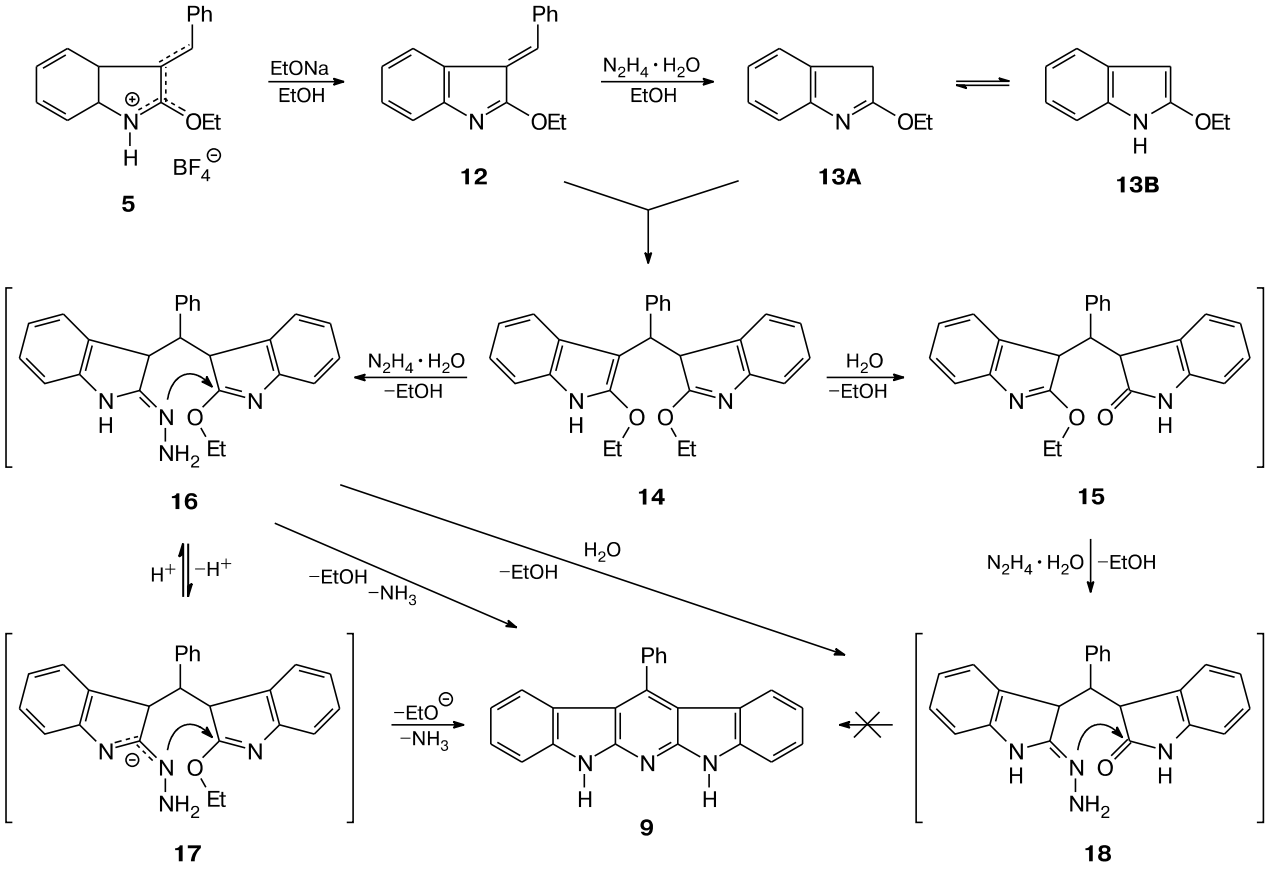
We propose a hypothetical scheme for the formation of pyridodiindole **9** (Scheme 2). The starting lactim ether **12** generated by decomposition of tetrafluoroborate **5** is a mixture of *E*-/*Z*-stereoisomers in a very unequal ratio (^{1}H NMR). The identification of the major isomer from spectroscopic data for the *E*- and *Z*-isomers of 3-benzylideneoxindole proved to be inconclusive because their spectroscopic characteristics differ only slightly,[13—15] except for the chemical shifts of the signals for the *ortho*-protons of the benzylidene group (δ 8.28 for *Z*-isomer and δ 7.62 for *E*-isomer[16]). This agrees well with δ 7.64 found by us for the major isomer of compound **12**. The actual configuration of this isomer was unambiguously determined by a NOESY experiment that revealed the Overhauser effect between the *ortho*-protons of the phenyl substituent and the indole H(4) proton, which are spatially close to each other: by analogy with the *E*-isomer of 3-benzylideneoxindole in the *twist*(49°)-conformation of the phenyl group, they are spaced at 2.48 Å (see Ref. 16). The presence of a small impurity of the *Z*-isomer in compound **12** is evident from a triplet and a quartet for the group —OCH_2Me in the ^{1}H NMR spectrum, which are shifted upfield by 0.10 and 0.05 ppm, respectively, compared to analogous signals for the *E*-isomer. The *E*/*Z* ratio of compound **12** is ~13 : 1.

Tetrafluoroborate **5** was treated with an equimolar amount of EtONa and the resulting lactim ether **12** was used *in situ* in a reaction with hydrazine hydrate. During the condensation, the reactants underwent a number of hypothetical transformations (Scheme 2) leading to pyridodiindole **9**. It is not improbable, however, that the sequence of some steps can be different or they can occur simultaneously, involving prototropic tautomers **13A** ⇄ **13B**.[17,18]

Apparently, the first step of this reaction is partial retro-crotonic decomposition of the starting compound into benzaldehyde (identified as 2,4-dinitrophenylhydrazone in a model experiment) and unsubstituted lactim ether **13**. The latter is unstable and known to react as either or both of its tautomers (**13A** and **13B**) at the CH_2/CH and lactim ether fragments with nucleophiles, electrophiles, and unsaturated compounds. In addition, it can undergo self-condensation, *e.g.*, into indirubin.[19—21] Indirubin was detected by TLC among the reaction products obtained from hydrazine hydrate or phenylhydrazine and lactim ether **12**, which provides indirect evidence for its retro-crotonic decomposition. Possible cleavage of the exocyclic double bond of the arylidene group in a series of 3-substituted indoles has been noted earlier.[11]

Having an active CH_2 group, lactim ether **13** easily adds to the double bond of the starting ylidene derivative **12** to give compound **14** containing two indole moieties, in accord with similar transformations of such indole derivatives in the Michael reaction.[12,22,23] Since compound **14** contains two lactim ether fragments, its reac-

Scheme 2



tion with hydrazine hydrate can follow two pathways: (1) hydrolysis of one lactim ether to lactam **15** and (2) replacement of the ethoxy group by the hydrazine residue, giving rise to compound **16**. However, the latter pathway seems to be preferred because hydrazine is a stronger nucleophile than water. The presence of a reactive amidrazone fragment in the indole ring of compound **16**, which becomes even more nucleophilic in the anionic form, enables the imine N atom to attack the neighboring lactim C atom with elimination of the ethoxy group. This results in closure of the pyridine ring, with an ammonia molecule being released.

Structure **18**, even though formed from precursors **15** and/or **16**, can hardly undergo cyclization according to available data on the lowered reactivity of the carbonyl group in the oxindole structure.[11]

To find out whether the aforementioned transformations are of general character, we also used 3-(4-bromobenzylidene)-2-ethoxyindoleninium tetrafluoroborate (**6**) and 2-ethoxy-3-(4-methoxybenzylidene)indoleninium tetrafluoroborate (**7**) in reactions with hydrazine hydrate. Compounds **6** and **7** were prepared from 3-arylideneoxindoles **3** and **4**, respectively, as described[1] for benzylidene analog **5**. The yields of the corresponding bromophenyl- and methoxyphenylpyridodiindoles **10** and **11** were as low as that of phenylpyridodiindole **9**. The low yields of the target pyridodiindoles **9**—**11** and the formation of many minor by-products (TLC) are due to the formation of several intermediates during the condensation that are comparable in reactivity and complicate the desired process.

To sum up, our method for the synthesis of 5*H*,7*H*-pyrido[2,3-*b*:6,5-*b*´]diindoles involves 3-arylidene-2-ethoxyindolenines as the starting materials, which is fundamentally different from a previous approach.[10—12] In our case, the closure of the pyridine ring proceeds by a nucleophilic attack of the hydrazino group that has been introduced into the indolenine structure under the action of hydrazine hydrate. Our method affords earlier unknown *N*(5),*N*(7)-unsubstituted analogs **9**—**11** of this heterocyclic system.

Experimental

Mass spectra were measured on a Thermo DFS instrument (EI, 70 eV, direct inlet probe). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 and Bruker AV-600 spectrometers;

the following solvents (and their signals as the internal standards) were used: DMSO-d_6 (δ_H 2.50, δ_C 39.50) for compounds **9**—**11** and $CDCl_3$ (δ_H 7.24, δ_C 76.91) for compound **12**. The course of the reactions was monitored and the purity of the products was checked by TLC on Silufol UV-254 plates with EtOAc—$CHCl_3$ (1 : 1 and 1 : 3) as an eluent; spots were visualized under UV light.

(*E*)-3-Benzylidene-2-ethoxyindolenine (12). A 50% aqueous solution of K_2CO_3 was added dropwise at 0—5 °C to a stirred solution of tetrafluoroborate **5** (5.0 g, 14.8 mmol) in CH_2Cl_2 (50 mL) to pH 8. The mixture was stirred for 0.5 h and then water (100 mL) was added. The organic phase was separated and the organic material from the aqueous phase was extracted with CH_2Cl_2 (4×30 mL). The combined organic extract was washed with water to pH 6, dried over $MgSO_4$, concentrated to dryness on a vacuum evaporator, and desiccated *in vacuo* over P_2O_5 and KOH. Yield 2.53 g (68%), m.p. 75—79 °C. Found (%): C, 81.29, 81.16; H, 5.81, 5.98; N, 5.68, 5.71. $C_{17}H_{15}N_3O$. Calculated (%): C, 81.90; H, 6.06; N, 5.62. MS, m/z (I_{rel} (%)): 249 $[M]^+$ (88), 221 (83), 220 $[M - C_2H_5]^+$ (100), 193 (46), 165 (46), 144 (41), 105 (12). HRMS: found: m/z 249.1147 $[M]^+$; $C_{17}H_{15}N_3O$; calculated: M = 249.1148. ^{1}H NMR (600 MHz), δ: 1.48 (t, 3 H, Me, ^3J = 7.1 Hz); 4.55 (q, 2 H, CH_2, ^3J = 7.1 Hz); 6.88 (ddd, 1 H, H(5), ^3J = 7.7 Hz, ^3J = 7.4 Hz, ^4J = 0.9 Hz); 7.21 (ddd, 1 H, H(6), ^3J = 7.7 Hz, ^3J = 7.6 Hz, ^4J = 0.8 Hz); 7.27 (d, 1 H, H(7), ^3J = 7.6 Hz); 7.41 (t, 1 H, *p*-H, Ph, ^3J = 7.3 Hz); 7.45 (t, 2 H, *m*-H, Ph, ^3J = 7.3 Hz); 7.57 (d, 1 H, H(4), ^3J = 7.6 Hz); 7.61 (s, 1 H, =CH); 7.64 (d, 2 H, *o*-H, Ph, ^3J = 7.3 Hz). ^{13}C NMR (125 MHz), δ: 14.39 (Me); 64.89 (CH_2); 118.28 (C(7)); 122.11 (C(4)); 122.79 (C(5)); 126.42 (C(3)); 128.49 (*m*-C); 129.37 (*o*-C); 129.48 (*p*-C); 129.66 (C(6)); 130.11 (*i*-C); 134.65 (C(3a)), 135.53 (=CH); 154.26 (C(7a)), 171.60 (C(2)).

12-Phenyl-5*H*,7*H*-pyrido[2,3-*b*:6,5-*b*´]diindole (9). Tetrafluoroborate **5** (3.0 g, 8.9 mmol) was added in portions at 0—5 °C to a stirred solution of EtONa prepared from metallic sodium (0.21 g, 8.9 mg-atom) and anhydrous ethanol (40 mL). Then hydrazine hydrate (0.52 g, 10 mmol) was added. The mixture was warmed to 20 °C and then refluxed for 6 h. On cooling, the precipitate of $NaBF_4$ was filtered off, the filtrate was concentrated to dryness *in vacuo* on a rotary evaporator at 50 °C. The yield of crude product **9** containing several minor compounds (TLC) was 2.5 g.

Part of this product (157 mg) was separated by preparative TLC on Silufol UV-254 plates in EtOAc—$CHCl_3$ (1 : 1). The UV-luminescent zone with $R_f \approx 0.6$ was collected. The individual product was extracted with hot ethanol. The extract was concentrated *in vacuo* at 50 °C. The yield of compound **9** was 22 mg (23% with respect to the starting tetrafluoroborate **5**), m.p. 309—311 °C (from $CHCl_3$). Found (%): C, 71.18, 70.36; H, 4.07, 4.01; N, 10.73, 10.71. $2C_{23}H_{15}N_3 \cdot CHCl_3$. Calculated (%): C, 71.71; H, 3.84; N, 10.68. MS, m/z (I_{rel} (%)): 333 $[M]^+$ (100), 332 $[M - H]^+$ (22), 331 $[M - 2H]^+$ (22), 166 (8). HRMS: found: m/z 333.1258 $[M]^+$; $C_{23}H_{15}N_3$; calculated: M = 333.1261. ^{1}H NMR (600 MHz), δ: 6.909 (ddd, 2 H, H(2), H(10), ^3J = 7.9 Hz, ^3J = 7.95 Hz, ^4J = 0.6 Hz); 6.958 (dd, 2 H, H(1), H(11), ^3J = 7.9 Hz, ^4J = 1.0 Hz); 7.281 (ddd, 2 H, H(3), H(9), ^3J = 8.0 Hz, ^3J = 7.95 Hz, ^4J = 0.7 Hz); 7.456 (dt, 2 H, H(4), H(8), ^3J = 8.0 Hz, ^4J = 0.6 Hz, ^4J = 0.6 Hz); 7.64—7.67 (m, 2 H, *o*-H, Ph); 7.69—7.73 (m, 1 H, *p*-H, Ph); 7.73—7.77 (m, 2 H, *m*-H, Ph); 11.783 (s, 2 H, NH). ^{13}C NMR (125 MHz), δ: 107.966 (C(11b), C(12a)); 110.770 (C(4), C(8)); 118.847 (C(2), C(10)); 120.223 (C(1), C(2)); 121.258 (C(11a), C(12b)); 124.607 (C(3), C(9)); 128.173 (*o*-C); 128.735 (*p*-C); 129.324 (*m*-C); 137.239 (*ipso*-C); 138.461 (C(4a), C(7a)); 139.258 (C(12); 151.374 (C(5a), C(6a)).

3-(4-Bromobenzylidene)-2-ethoxyindoleninium tetrafluoroborate (6) and 2-ethoxy-3-(4-methoxybenzylidene)indoleninium tetrafluoroborate (7) were obtained by alkylation of appropriate 3-arylideneindolinones **3** and **4** with Et_3O—BF_4 as described[1] for compound **5**.

Compound 6, m.p. 157—160 °C. Found (%): C, 48.97, 48.34; H, 3.49, 3.32; Br, 19.40, 19.80; F, 18.29, 18.44; N, 3.46, 3.68. $C_{17}H_{15}BrNO \cdot BF_4$. Calculated (%): C, 49.07; H, 3.63; Br, 19.21; F, 18.27; N, 3.37.

Compound 7, m.p. 187—190 °C. Found (%): C, 58.79, 58.48; H, 4.90, 4.88; F, 20.65, 20.35; N, 4.02, 4.12. $C_{18}H_{18}NO_2 \cdot BF_4$. Calculated (%): C, 58.88; H, 4.94; F, 20.70; N, 3.82.

12-(4-Bromophenyl)-5*H*,7*H*-pyrido[2,3-*b*:6,5-*b*´]diindole (10) was obtained from tetrafluoroborate **6** as described for compound **9**. Yield 23%, m.p. 297—299 °C (from EtOH). Found (%): C, 67.00, 67.00; H, 3.62, 3.73; Br, 19.14, 19.06; N, 9.87, 9.82. $C_{23}H_{14}BrN_3$. Calculated (%): C, 67.00; H, 3.42; Br, 19.38; N, 10.19. MS, m/z (I_{rel} (%)): 413 $[M]^+$ (99), 411 $[M]^+$ (100), 332 $[M - Br]^+$ (13), 331 (33), 330 (13), 166 (22), 165 (20), 149 (24). HRMS: found: m/z 411.0362 $[M]^+$; $C_{23}H_{14}Br^{79}N_3$; calculated: M = 411.0366. ^{1}H NMR (400 MHz), δ: 6.94 (dd, 2 H, ^3J = 7.0 Hz, ^3J = 7.8 Hz); 7.08 (d, 2 H, ^3J = 7.2 Hz); 7.29 (dd, 2 H, ^3J = 7.0 Hz, ^3J = 7.8 Hz); 7.46 (d, 2 H, ^3J = 8.0 Hz); 7.63 (d, 2 H, ^3J = 8.0 Hz); 7.93 (d, 2 H, ^3J = 7.5 Hz); 11.83 (s, 2 H, NH). ^{13}C NMR (100 MHz), δ: 108.12; 111.23; 119.36; 120.49; 121.38; 122.44; 125.11; 130.96; 132.74; 136.80; 138.13; 138.85; 151.68.

12-(4-Methoxyphenyl)-5*H*,7*H*-pyrido[2,3-*b*:6,5-*b*´]diindole (11) was obtained from tetrafluoroborate **7** as described for compound **9**. Yield 23%, m.p. 273—279 °C (from EtOH). Found (%): C, 79.25, 78.87; H, 5.09, 5.15; N, 11.06, 10.70. $C_{24}H_{17}N_3O$. Calculated (%): C, 79.32; H, 4.72; N, 11.56. MS, m/z (I_{rel} (%)): 363 $[M]^+$ (100), 333 $[M - OCH_2]^+$ (13), 3.19 (12), 318 (14). HRMS: found: m/z 363.1365 $[M]^+$; $C_{24}H_{17}N_3O$; calculated: M = 363.1366. ^{1}H NMR (400 MHz), δ: 3.95 (s, 3 H, Me); 6.93 (dd, 2 H, ^3J = 7.3 Hz, ^3J = 7.5 Hz); 7.08 (d, 2 H, ^3J = 7.8 Hz); 7.28 (t, 2 H, ^3J = 7.3 Hz); 7.29 (d, 2 H, ^3J = 7.9 Hz); 7.45 (d, 2 H, ^3J = 7.9 Hz); 7.58 (d, 2 H, ^3J = 8.4 Hz); 11.76 (s, 2 H, NH). ^{13}C NMR (100 MHz), δ: 55.26; 108.31; 110.76; 114.64; 118.87; 120.34; 121.41; 124.57; 129.11; 129.64; 138.45; 139.34; 151.42; 159.47.

Single-crystal X-ray diffraction study of 12-phenyl-5*H*,7*H*-pyrido[2,3-*b*:6,5-*b*´]diindole (9) was carried out on a Bruker Kappa APEX II CCD diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, 173 K, φ,ω scan mode, 2θ < 52.74°). Triclinic pink crystals, $2(C_{23}H_{15}N_3) + CHCl_3$, M = 786.13, space group $P\bar{1}$, a = 12.0759(4) Å, b = 12.9906(5) Å, c = 13.5779(5) Å, α = 104.931(2)°, β = 111.853(2)°, γ = 92.890(2)°, V = 1884.60(12) Å^3, Z = 2, D_{calc} = 1.385 g cm^{-3}, μ = 0.288 mm^{-1}. The intensities of 29 187 reflections from a single crystal (0.14×0.15×0.60 mm) were measured. The number of independent reflections was 7695 (R_{int} = 0.0432); the number of reflections with $I > 2\sigma(I)$ was 5742. The number of parameters refined was 549, R = 0.0677 ($I > 2\sigma(I)$), wR_2 = 0.2000, GOOF = 1.067 (for all reflections). An absorption correction was applied with the SADABS program (T_{min}/T_{max} = 0.786/0.862). The structure was solved by direct methods. The coordinates and thermal parameters of the non-hydrogen atoms were refined anisotropically by the full-

matrix least-squares method. The amino H atoms were located in difference electron-density maps and refined isotropically. The other H atoms were refined using a riding model. The solvate $CHCl_3$ molecule is disordered over two positions in a ratio of 0.604(4) : 0.396(4). All calculations were performed with the SHELXTL program package. Atomic coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 824888).

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Received May 19, 2011;
in revised form October 11, 2011