New push-pull systems based on indolo[3,2-*b*]carbazole and 1,2,4,5-tetrazine: synthesis, photophysical, and charge transport properties

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5,11-Dihydroindolo[3,2-*b*]carbazoles were for the first time modified with acceptor 1,2,4,5-tetrazine fragments. The photophysical and charge-transport properties of the synthesized donor-acceptor heterocyclic systems were studied. It was shown that the introduction of the 1,2,4,5-tetrazine moieties makes it possible to increase the hole and electron mobility by one and two orders of magnitude, respectively, as compared to analogous 5,11-dihydroindolo-[3,2-*b*]carbazole derivatives studied previously.

Key words: 1,2,4,5-tetrazines, nucleophilic substitution, indolo[3,2-*b*]carbazole, push-pull systems.

Recently, the 5,11-dihydroindolo[3,2-*b*]carbazole (ICZ) scaffold has been widely used as a constituent of novel organic compounds used in the design of functional materials for molecular electronics. Various ICZ derivatives are of interest as semiconductor materials with hole conductivity for solar cells[1] or field-effect transistors,[2,3] dyes for sensitized solar cells (Grätzel cells),[4] light-emitting diodes,[5] as well as electrochromic[6,7] or fluorescent materials with sensor properties.[8,9] Previous studies of photophysical and charge transport properties of 5,11-dialkyl-6,12-diaryl(hetaryl)-5,11-dihydroindolo-[3,2-*b*]carbazoles[10,11] revealed a considerable promise of search for novel functional materials based on this class of compounds.

1,2,4,5-Tetrazines are conjugated electrochemically active molecules that possess strong electron-withdrawing properties. They are characterized by absorption in the visible region resulting from n—π* electronic transitions and can undergo reversible reduction to radical anions.[12] These features offer prospects for the search for novel conductive organic compounds and materials for electronic devices and sensors in this class of chemical substances.

Compounds containing the donor ICZ fragment conjugated with acceptor tetrazine rings are unavailable at the moment. However, such hybrid molecules are of interest as potential building blocks for materials with unique photophysical and electronic properties. To design the systems in question, in this work we propose to modify 1,2,4,5-tetrazine using typical reactions of this compound, *viz.*, nucleophilic substitution of leaving azolyl groups[13] under the action of ICZ bearing nucleophilic substituents. Reduction of three nitro derivatives of ICZ, namely, compounds **1** and **2a,b**,[14] afforded new amino derivatives **3** and **4a,b**, respectively, in high yields of 74—82% (Scheme 1).

Further reactions of amines **3** and **4a,b** with 3,6-bis-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (DPTz), which was synthesized following a known procedure,[15] in toluene at 60 °C respectively gave compounds **5** and **6a,b** (Scheme 2) representing the substitution products of one 3,5-dimethylpyrazolyl group in the tetrazine ring of DPTz.

Compounds **5** and **6a,b** bear a mobile NH proton capable of undergoing tautomeric transitions. To study the effect of this proton on the properties of compounds **5** and **6a,b**, we attempted to synthesize an *N*-alkylated analogue to compound **5** containing no mobile proton. To this end, compound **3** was acylated and then the acetyl group was reduced to ethyl one under the action of alu-

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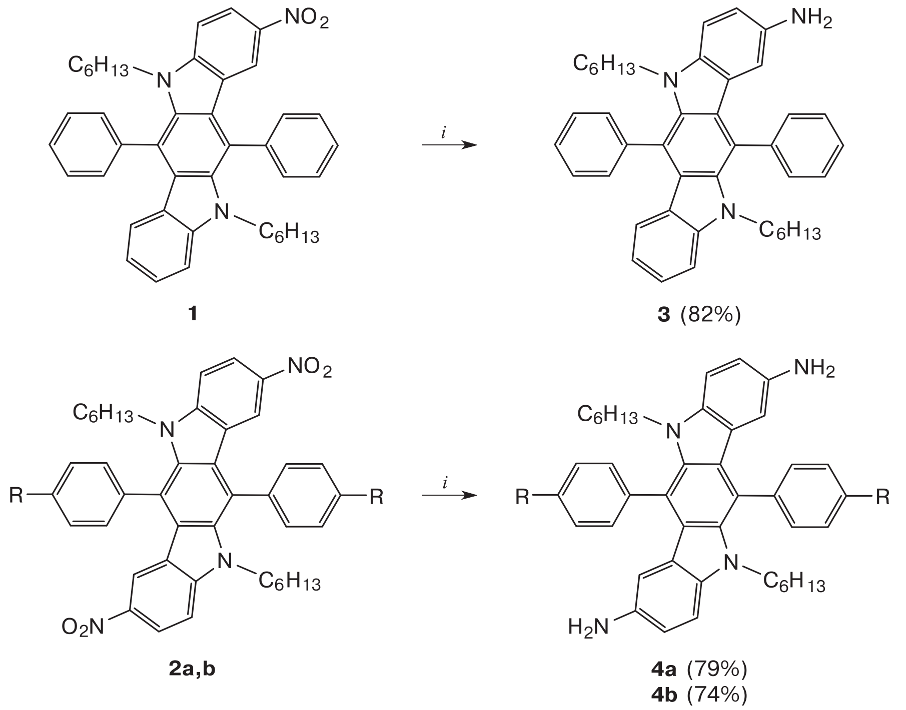
* Dedicated to Academician of the Russian Academy of Sciences V. N. Charushin on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1109—1117, June, 2021.

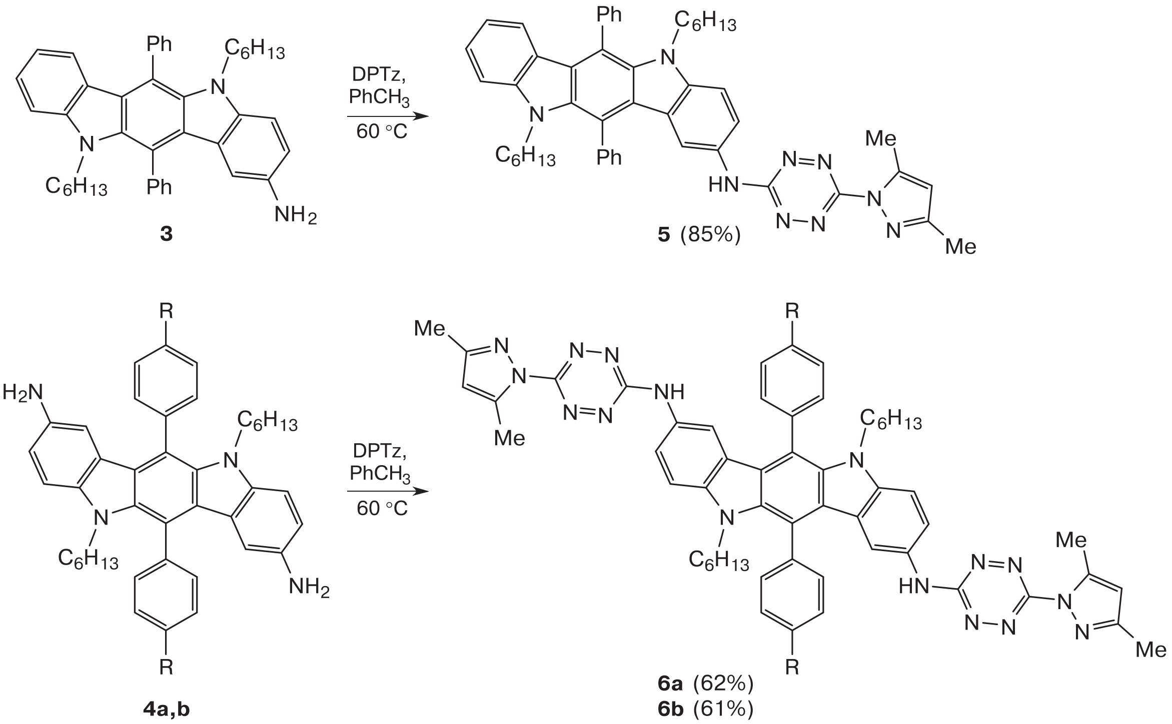
Scheme 1

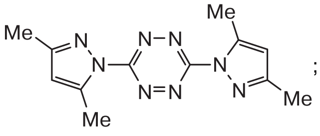


R = F (**a**), OC$_6$H$_{13}$ (**b**)

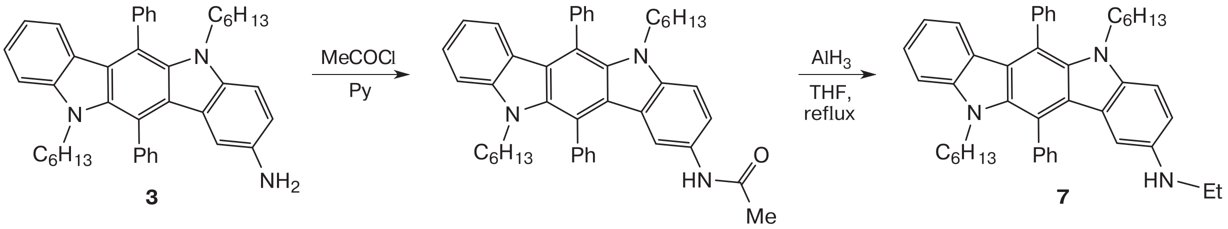
Reactants and conditions. *i*. Zn + HCl (aq.)/THF, reflux 1 h.

Scheme 2



DPTz =  ; **4,6:** R = F (**a**), OC$_6$H$_{13}$ (**b**)

Scheme 3

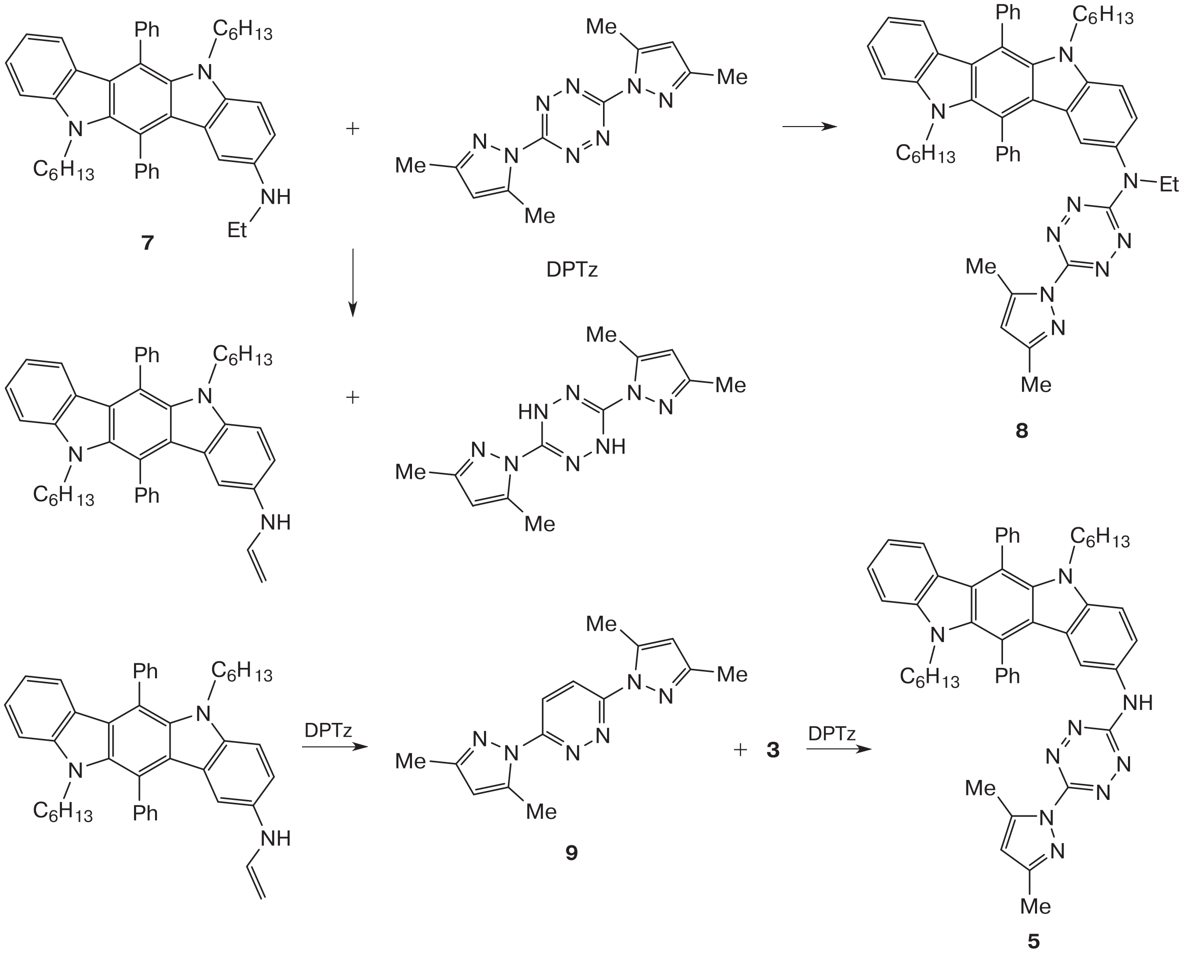


minum hydride to give the *N*-ethylated derivative **7** (Scheme 3).

We assumed that the reaction of compound **7** with DPTz in toluene under reflux will result in a substitution product similar to compounds **5** and **6**; however, our attempt failed. According to TLC data, the reaction mixture contained only the starting compounds and a small amount of side products. However, the reaction of **7** with DPTz did proceed in mesitylene under reflux for 10 h or when the starting compounds were fused under solvent-free conditions. According to ^{1}H NMR and LC-HRMS data, in both cases the major product was compound **5** containing no ethyl substituent at the amine nitrogen. Based on the LC-HRMS data, the reaction mixture also contained a very small amount of the target product **8**; however, we failed to isolate it in pure form. The reaction afforded not only compounds **5** and **8**, but also a colorless product identified by ^{1}H NMR and LC-HRMS as pyridazine **9** (Scheme 4).

Probably, the ethyl fragment in compound **7** is transformed to vinyl one under the action of the starting tetrazine. Subsequent interaction of the vinyl group with DPTz

Scheme 4



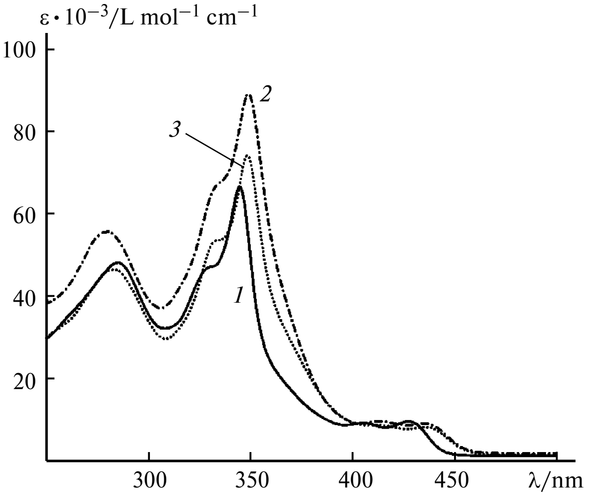


Fig. 1. Absorption spectra of solutions of compounds **5** (*1*), **6a** (*2*), and **6b** (*3*) in $CHCl_3$.

results in the formation of dihydropyridazine and its aromatization upon elimination of aminoindolocarbazole **3**. Then, the de-ethylated amine **3** reacted with DPTz in the reaction mixture to give compound **5**.

We studied the photophysical and electronic properties of products **5** and **6a**,**b**. The electronic absorption spectra of these compounds in $CHCl_3$ solution recorded at room temperature are shown in Fig. 1. Electronic absorption, which mainly occurs in the range of 310—400 nm, originates from intramolecular π—π* charge transfer from the donor indolo[3,2-*b*]carbazole to the acceptor fragment. The molar extinction coefficients ε at the absorption maxima calculated from these spectra are listed in Table 1.

Compounds **5, 6a** can form nanometer-thin solid layers (films) by solution coating on horizontally arranged substrates. To study the possibility to use them in the design of organic electronic devices, we studied the optical, electronic, charge transport properties, and the surface morphology of the films.

The electronic absorption spectra of thin films of compounds **5** and **6a** in the visible region (see Fig. 2) exhibit a bathochromic shift of the absorption maximum by 1 and 10 nm, respectively. The optical band gap E_g was evaluated from the long-wavelength absorption edge (see Table 1).

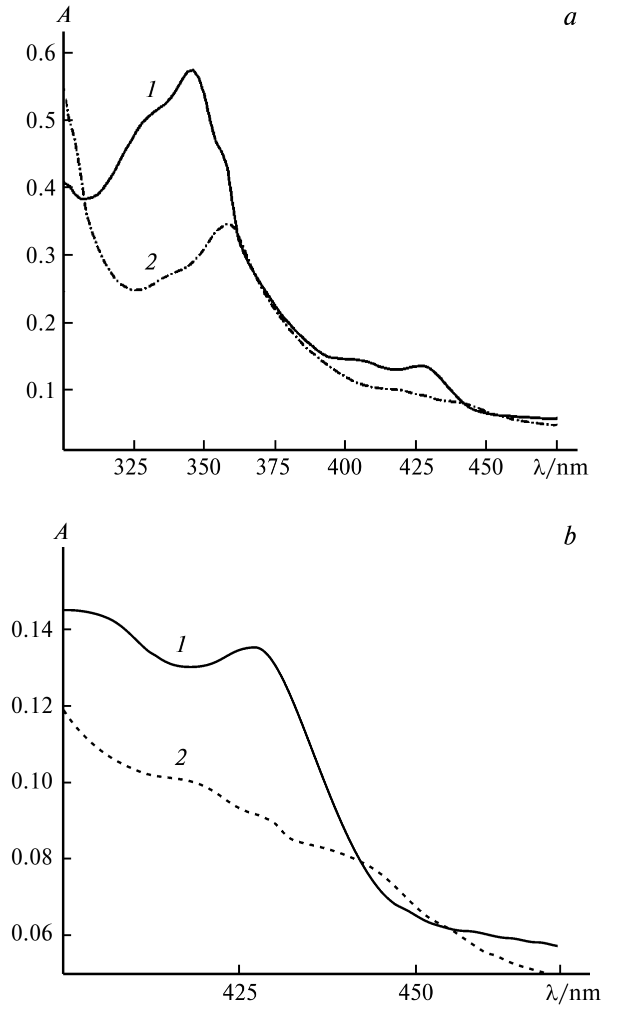


Fig. 2. Absorption spectra of thin films of compounds **5** (*1*) and **6a** (*2*) prepared by spin coating from solutions of these compounds (C = 10 mg L^{-1}) in $CHCl_3$ (*a*) and magnified fragments of these spectra (*b*); film thickness is ~100 nm.

Table 1. Optical and electronic properties of compounds **5** and **6a**,**b**

Compound	λ_1/nm	$\varepsilon \cdot 10^{-3}$ /L mol^{-1} cm^{-1}	λ_2	λ_3	E$_g$	E$_{HOMO}$	E$_{LUMO}$
			nm		eV		
5	345	67.2	346	449	2.76	−5.32	−2.56
6a	349	91.3	359	494	2.51	−5.26	−2.75
6b	348	74.2	—	—	—	—	—

λ_1 is the absorption maximum and the extinction coefficient (ε) measured in $CHCl_3$ solution; λ_2 is the absorption maximum for the thin film, λ_3 is the long-wavelength absorption edge; E_g is the optical band gap calculated from the absorption edge using the expression $E_g = 1240/\lambda_3$ (nm); E_{HOMO} is the energy of the highest occupied molecular orbital (HOMO) determined from the UV photoelectron spectra; E_{LUMO} is the energy of the lowest unoccupied molecular orbital (LUMO) calculated from the equation $E_{LUMO} = E_g + E_{HOMO}$.

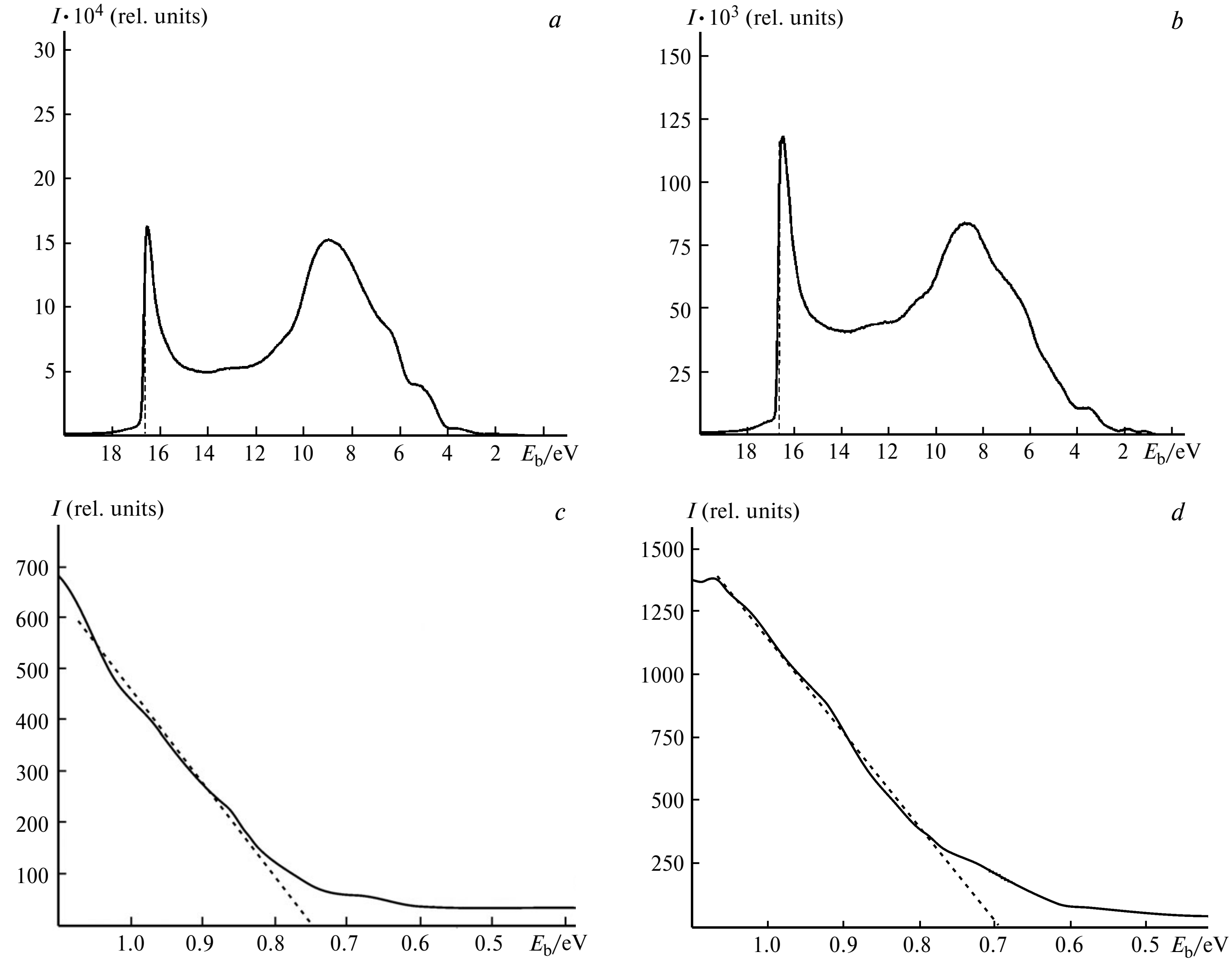


Fig. 3. UV photoelectron spectra of thin films prepared by spin coating from solutions of compounds **5** (*a*) and **6a** (*b*) in $CHCl_3$ and magnified fragments of the spectra of these compounds (*c*) and (*d*), respectively; E_b is the binding energy; UV means excitation by photons with an energy of 21.21 eV (HeI).

The UV photoelectron spectra of thin films of compounds **5** (*a*) and **6a** (*b*) are shown in Fig. 3. They were used to determine positions of the energy levels of the highest occupied molecular orbitals (HOMOs) of these compounds.

The X-ray diffraction patterns (see Fig. 4) of untreated thin films of compounds **5** and **6a** (curves *1*) exhibit no diffraction reflections and correspond to amorphous state of the films. Heat treatment (curves *2*) was followed by the appearance of broadened peaks indicating an increase in the degree of crystallinity in these films.

To assess the charge transport properties of the new compounds, the charge carrier mobility in thin layers of compound **5** was measured using the metal—insulator—semiconductor charge extraction at linear increasing voltage (MIS-CELIV) method. The results obtained are presented in Table 2. The MIS-CELIV method involves the measurement of a transient current signal at linearly increasing voltage applied to the sample of a MIS structure. The conditions of our experiments were documented elsewhere.[16—18] The electron and hole mobility in the layer of compound **5** is rather high, *viz.*, of the order of 10^{-4} cm^2 V^{-1} s^{-1} (see Table 2), being one or two orders of magnitude higher than the mobility in thieno[3,2-*b*]indole,[16] indolo[3,2-*b*]carbazoles,[11,19] and in new boron-containing indolocarbazole complexes.[2] The charge carrier mobility in indolocarbazoles depends on the character of molecular packing in the layer,[20] which is in turn determined by the molecular structure and by the film fabrication method and conditions. We believe that the chain length in the alkyl substituent in molecule **5** specifies the average intermolecular distance and mutual arrangement of molecules in the mainly amorphous layers. For instance, a study of oligomeric molecules with the same core showed[18] that a relatively high charge carrier mobility is achieved at the optimum chain length in the alkyl substituent.

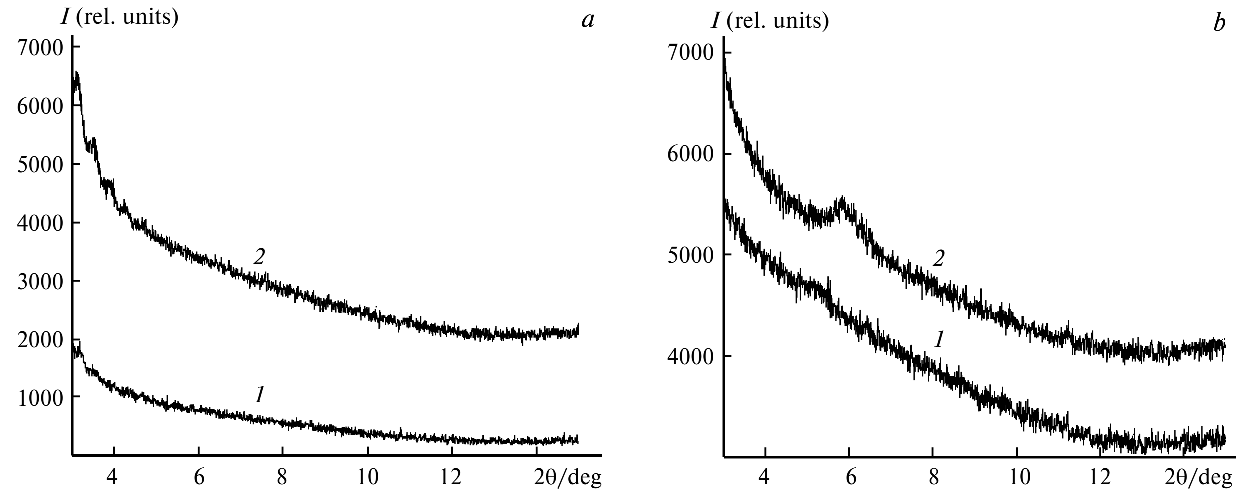


Fig. 4. X-ray diffracrion patterns of thin films of compounds **5** (*a*) and **6a** (*b*) on glassy substrate before (*1*) and after (*2*) heat treatment for 10 min at 90 °C.

From the data of Table 2 it follows that the charge carrier mobility in the film is strongly influenced by the nature of the solvent used to prepare the film. The more volatile solvent (chloroform) evaporates so rapidly that molecules of compound **5** have no time to reach a thermodynamic equilibrium, which leads to scatter in the electronic energy distribution of the HOMO and LUMO levels and, as a consequence, certain molecules act as deep charge carrier traps. If the solvent evaporates relatively slowly (dimethylsulfoxide), a larger number of molecules of compound **5** go to the thermodynamically equilibrium state and, as a consequence, the scatter of the MO levels decreases, while the charge carrier mobility increases.

One more feature of charge transport in the films of compound **5**, which is of importance for the design of electronic devices, consists in that the electron and hole mobilities are comparable in magnitude (see Table 2). For instance, balanced electron and hole mobilities are necessary for operation of functional layers in light-emitting diodes and solar cells.

Summing up, we demonstrated the possibility of engineering new push-pull heterocyclic molecules containing the 5,11-dihydroindolo[3,2-*b*]carbazole scaffold and the 1,2,4,5-tetrazine moiety using nucleophilic substitution of heterocyclic leaving groups in the 1,2,4,5-tetrazine ring under the action of amino derivatives of ICZ. We also studied the optical, electronic, and charge-transport properties of the new compounds. It was found that compound **5** exhibits ambipolar conductivity owing to the presence of both donor (indolocarbazole) and acceptor (tetrazine) fragments that act as transport centers for holes and electrons, respectively. It was established that the introduction of the 1,2,4,5-tetrazine moieties allows the hole and electron mobility to increase by one and two orders of magnitude, respectively, compared to those in the previously studied related derivatives of 5,11-dihydroindolo[3,2-*b*]carbazole.

Table 2. Charge carrier mobility in layers prepared from different solutions of compound **5**

Solvent	T/°C	$\mu \cdot 10^{-4}$/cm^2 V^{-1} s^{-1}	
		electrons	holes
Chloroform	61.2	0.6	1.1
DMSO	189	6.8	6.6

T is the boiling point and μ is the charge carrier mobility.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer operating at 400 and 100 MHz, respectively, in $CDCl_3$ or DMSO-d$_6$ with tetramethylsilane as an internal reference. High-resolution mass spectra of solutions in CH_3CN were recorded on a Bruker maXis impact HD quadrupole time-of-flight mass spectrometer (positive ion mode, electrospray ionization). Elemental analysis was performed on a 2400 Series II CHNS elemental analyzer (Perkin—Elmer, USA). Melting points were determined on a Boetius apparatus. The course of the reactions and the purity of the compounds synthesized was monitored by TLC using Silufol plates with PhH—MeCN (1 : 1) mixture as eluent. Electronic absorption spectra of solutions were recorded on a Shimadzu UV-2600 (Japan) double-beam spectrophotometer. Electronic absorption spectra of thin layers in the visible region were recorded on a Shimadzu UV-3101PC (Japan) double-beam spectrophotometer. The layer thickness was measured using an Alpha-Step D-100 stylus profiler (KLA tencor, USA). The energy of the HOMO level was determined by UV photoelectron spectroscopy on an Axis Ultra DLD spectrometer (Kratos Analytical, United Kingdom). The X-ray diffraction patterns of thin films were collected on an EMPYREAN X-ray diffractometer (PANalytical B.V., The Netherlands) in air at room temperature (Cu-Kα radiation, 2θ scan range of 3—15 deg). Thin layers of compounds **5** and **6a** were prepared by spin coating from solutions in chloroform ($C = 10$ mg L^{-1}; centrifugation at 1000 rev min^{-1} for 1 min).

The carrier mobility was determined by the MIS—CELIV method using sandwich-type samples prepared as follows. A glassy substrate was coated with an ITO (mixture of In_2O_3 and SnO_2) conductive layer and then with a 70-nm SiO_2 layer. Then, it was successively coated with a layer of the compound under study (layer thickness $d = 100$ nm) and with an Al layer ($d = 80$ nm) as a counterelectrode. The SiO_2 insulating layer played the role of the blocking layer for both types of charge carriers, *i.e.*, it precluded injection of the charge carriers from ITO. When measuring the transient hole current, a positive potential linearly increasing at a rate of $A = 5 \cdot 10^4$ V s^{-1} was applied to ITO; this was accompanied by the extraction of holes at the Al electrode. To measure the electron mobility, the polarity of the potential applied to the electrode was reversed. The characteristic time (t_{max}) corresponding to the maximum transient conduction current was determined using the current signal detected at the load resistor of a DL-Analog Discovery (Digilent Co.) oscilloscope. The carrier mobility was calculated using the expression $\mu = 2d^2/(At^2_{max})$.[18]

Compounds **1**, **2a**,**b**[14] and 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (DPTz)[15] were synthesized following known procedures. Commercially available reactants and solvents were used without additional purification.

Reduction of nitro derivatives 1 and 2a,b to amino derivatives 3 and 4a,b, respectively (general procedure). To a vigorously stirred mixture of 2,8-dinitro derivative **2** (1 mmol) and zinc powder (1.3 g, 20 mmol) in THF (40 mL), 12 *M* HCl (5.2 mL, 62.4 mmol) was added dropwise. The reaction mixture was refluxed with stirring until complete dissolution of zinc. Then, 5% NaOH (100 mL) was added and the product was extracted with CH_2Cl_2 (3×20 mL). The solvent was evaporated at a reduced pressure and a solid residue thus obtained was dissolved in THF (3 mL), and ethanol (10 mL) was added. The precipitate (amino derivative) was filtered off, washed with ethanol (2×2 mL), and dried at 110 °C. Reduction of the mononitro derivative using this procedure involved treatment of compound **1** (310 mg, 0.5 mmol) with Zn powder (330 mg, 5 mmol) and 12 *M* HCl (1.3 mL, 15.6 mmol) in THF (10 mL).

5,11-Dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazol-2-amine (3). The yield was 243 mg (82%). M.p. 193—195 °C. $R_f = 0.71$ (with THF as eluent). Found (%): C, 85.32; H, 7.58; N, 6.98. $C_{42}H_{45}N_3$. Calculated (%): C, 85.24; H, 7.66; N, 7.10. ^1H NMR (C_6D_6, δ): 0.76—0.84 (m, 10 H, 2 CH_2CH_3); 0.95—1.01 (m, 4 H, 2 CH_2); 1.09—1.17 (m, 4 H, 2 CH_2); 1.40—1.47 (m, 4 H, 2 CH_2); 2.75 (br.s, 2 H, NH_2); 3.69—3.72 (m, 4 H, 2 NCH_2); 6.19 (d, 1 H, C(1)H, $J = 2.2$ Hz); 6.65 (dd, 1 H, C(3)H, $J_1 = 8.5$ Hz, $J_2 = 2.2$ Hz); 6.98—7.00, 7.03—7.04 (both m, 1 H each, C(8)H, C(9)H); 7.07 (d, 1 H, C(4)H, $J = 8.5$ Hz); 7.20 (d, 1 H, CH_{ICZ}, $J = 8.2$ Hz); 7.28—7.36 (m, 7 H, 6 CH_{Ph}, 1 CH_{ICZ}); 7.60—7.64 (m, 4 H, 4 CH_{Ph}). ^{13}C NMR (C_6D_6, δ): 14.20 (2 C), 22.88 (2 C), 26.65, 26.68, 28.86, 28.94, 31.72, 31.76, 44.66, 44.78, 108.72, 108.85, 109.20, 115.53, 118.47, 118.52, 123.05, 123.11, 123.34, 124.05, 124.63, 125.69, 127.89, 128.06, 128.31, 128.93 (2 C), 129.10 (2 C), 131.04 (2 C), 131.14 (2 C), 132.82, 133.91, 137.80, 139.20, 139.95, 139.97, 143.34.

6,12-Bis(4-fluorophenyl)-5,11-dihexyl-5,11-dihydroindolo-[3,2-*b*]carbazole-2,8-diamine (4a). The yield was 508 mg (79%). M.p. 274—275 °C. $R_f = 0.73$ (with THF as eluent). Found (%): C, 78.63; H, 7.12; N, 8.63. $C_{42}H_{44}F_2N_4$. Calculated (%): C, 78.47; H, 6.90; N, 8.72. ^1H NMR (C_6D_6, δ): 0.78—0.85 (m, 10 H, 2 CH_2CH_3); 0.94—1.00 (m, 4 H, 2 CH_2); 1.08—1.15 (m, 4 H, 2 CH_2); 1.35—1.41 (m, 4 H, 2 CH_2); 2.74 (br.s, 4 H, 2 NH_2); 3.61—3.64 (m, 4 H, 2 NCH_2); 6.16 (d, 2 H, C(1)H, C(7)H, $J = 2.2$ Hz); 6.65 (dd, 2 H, C(3)H, C(9)H, $J_1 = 8.5$ Hz, $J_2 = 2.2$ Hz); 6.94—6.98, 7.38—7.41 (both m, 4 H each, 8 CH_{Ar}); 7.06 (d, 2 H, C(4)H, C(10)H, $J = 8.5$ Hz). ^{13}C NMR (C_6D_6, δ): 14.17, 22.86, 26.73, 28.86, 31.75, 44.83, 108.91 (d, $J = 98.4$ Hz); 115.68 (d, 2 C, $J = 23.9$ Hz); 115.94, 117.36, 123.14, 124.51, 132.78 (d, 2 C, $J = 7.7$ Hz); 133.76, 135.80, 137.79, 139.34, 162.07, 164.03.

5,11-Dihexyl-6,12-bis(4-hexyloxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-diamine (4b). The yield was 597 mg (74%). M.p. 174—175 °C. $R_f = 0.75$ (with THF as eluent). Found (%): C, 80.11; H, 8.92; N, 6.76. $C_{54}H_{70}N_4O_2$. Calculated (%): C, 80.35; H, 8.74; N, 6.94. ^1H NMR (C_6D_6, δ): 0.84 (t, 6 H, 2 CH_3, $J = 7.3$ Hz); 0.88—0.93 (m, 10 H, 2 CH_2, 2 CH_3); 0.99—1.05 (m, 4 H, 2 CH_2); 1.12—1.19 (m, 4 H, 2 CH_2); 1.22—1.31 (m, 8 H, 4 CH_2); 1.36—1.42 (m, 4 H, 2 CH_2); 1.46—1.54 (m, 4 H, 2 CH_2); 1.67—1.72 (m, 4 H, 2 CH_2); 2.76 (br.s, 4 H, 2 NH_2); 3.78—3.81 (m, 8 H, 2 NCH_2, 2 OCH_2); 6.49 (d, 2 H, C(1)H, C(7)H, $J = 2.2$ Hz); 6.66 (dd, 2 H, C(3)H, C(9)H, $J_1 = 8.4$ Hz, $J_2 = 2.2$ Hz); 7.03, 7.58 (both d, 4 H each, 8 CH_{Ar}, $J = 8.6$ Hz); 7.10 (d, 2 H, C(4)H, C(10)H, $J = 8.4$ Hz).

Substitution of 3,5-dimethylpyrazolyl group in DPTz under the action of amines 3 and 4a,b (general procedure). To a solution of amine (0.5 mmol) in toluene (20 mL), DPTz (135 mg, 0.5 mmol in the case of amine **3** or 270 mg, 1 mmol in the case of diamines **4a,b**) was added. The reaction mixture was kept at 60 °C under stirring for 5 h and an additional 24 h at room temperature. The precipitate was filtered off. Product **5** was washed with CH_3CN. Compounds **6a,b** were recrystallized from DMF, washed with acetonitrile, and dried at a pressure of 15 mbar and at a temperature of 110 °C for 5 h.

***N*-[6-(3,5-Dimethylpyrazol-1-yl)-1,2,4,5-tetrazine-3-yl]-5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazol-2-amine (5).** The yield was 326 mg (85%). M.p. 211—213 °C. $R_f = 0.44$ (with CH_2Cl_2 as eluent). Found (%): C, 76.85; H, 6.89; N, 16.32. $C_{49}H_{51}N_9$. Calculated (%): C, 76.83; H, 6.71; N, 16.46. ^1H (DMSO-d_6, δ): 0.80—0.90 (m, 10 H, 2 CH_2CH_3); 1.04—1.12 (m, 4 H, 2 CH_2); 1.15—1.23 (m, 4 H, 2 CH_2); 1.35—1.48 (m, 4 H, 2 CH_2); 2.26, 2.48 (both s, 3 H each, 2 CH_3 in pyrazolyl); 3.74—3.82 (m, 4 H, 2 NCH_2); 6.24 (s, 1 H, C(4)H in pyrazolyl); 6.36 (d, 1 H, C(10)H, $J = 7.7$ Hz); 6.76 (dd, 1 H, C(8)H, $J_1 = 8.2$ Hz, $J_2 = 7.0$ Hz); 6.92 (d, 1 H, C(1)H, $J = 1.9$ Hz); 7.30 (dd, 1 H, C(9)H, $J_1 = 7.7$ Hz, $J_2 = 7.0$ Hz); 7.41 (d, 1 H, C(7)H, $J = 8.2$ Hz); 7.47 (d, 1 H, C(4)H, $J = 8.8$ Hz); 7.53 (dd, 1 H, C(3)H, $J_1 = 8.8$ Hz, $J_2 = 1.9$ Hz); 7.59—7.72 (m, 10 H, 2 Ph); 10.68 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6, δ): 12.33, 13.28, 13.73, 13.75, 21.91, 21.93, 25.60, 25.63, 28.14, 28.26, 30.71, 30.72, 43.65, 43.78, 108.63, 108.67, 108.72, 115.11, 117.71, 117.73, 117.90, 120.57, 121.60 (2 C), 122.02 (2 C), 122.13, 125.46, 128.21, 128.29, 128.33, 128.99 (2 C), 129.05 (2 C), 129.81 (2 C), 130.11 (2 C), 131.68, 132.11, 137.37, 137.97, 139.30, 141.40, 142.11, 150.16, 156.94, 160.41.

N^2,N^8-Bis[6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine-3-yl]-6,12-bis(4-fluorophenyl)-5,11-dihexyl-5,11-dihydroindolo-[3,2-*b*]carbazole-2,8-diamine (6a). The yield was 307 mg (62%). M.p. 334—335 °C. $R_f = 0.74$ (with EtOAc—C_6H_{14} (1 : 1) as eluent). Found (%): C, 67.78; H, 5.78; N, 22.61. $C_{56}H_{56}F_2N_{16}$.

Calculated (%): C, 67.86; H, 5.69; N, 22.61. ^{1}H NMR (DMSO-d_6, δ): 0.84 (t, 6 H, 2 CH_3, *J* = 7.3 Hz); 0.88—0.94 (m, 4 H, 2 CH_2); 1.07—1.13 (m, 4 H, 2 CH_2); 1.17—1.23 (m, 4 H, 2 CH_2); 1.39—1.49 (m, 4 H, 2 CH_2); 2.26, 2.50 (both s, 6 H each, 4 CH_3 in two pyrazolyls); 3.76—3.80 (m, 4 H, 2 NCH_2); 6.24 (s, 2 H, 2 C(4)H in two pyrazolyls); 7.05 (s, 2 H, C(1)H, C(7)H); 7.46—7.50 (m, 6 H, 4 CH_{Ar}, C(4)H, C(10)H); 7.62 (dd, 2 H, C(3)H, C(9)H, J_1 = 8.8 Hz, J_2 = 1.7 Hz); 7.71—7.74 (m, 4 H, 4 CH_{Ar}); 10.81 (br.s, 2 H, 2 NH). ^{13}C (DMSO-d_6, δ): 12.24, 13.28, 13.71, 21.97, 25.75, 28.24, 30.72, 43.89, 108.60, 108.90, 114.31, 116.13 (d, *J* = 21.2 Hz); 117.07, 120.22, 121.93 (d, 2 C, *J* = 14.8 Hz); 128.75, 131.93 (d, 2 C, *J* = 7.8 Hz); 132.42, 133.40 (d, *J* = 3.2 Hz); 139.25, 141.47, 150.15, 156.90, 160.25, 161.33, 163.29.

***N*^{2},*N*^{8}-Bis[6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine-3-yl]-5,11-dihexyl-6,12-bis(4-hexyloxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-diamine (6b).** The yield was 352 mg (61%). M.p. 285—286 °C. R_f = 0.86 (with EtOAc—C_6H_{14} (1 : 1) as eluent). Found (%): C, 70.63; H, 7.08; N, 19.23. $C_{68}H_{82}N_{16}O_2$. Calculated (%): C, 70.68; H, 7.15; N, 19.40. ^{1}H NMR (DMSO-d_6, δ): 0.83 (t, 6 H, 2 CH_3, *J* = 7.2 Hz); 0.88—0.93 (m, 10 H, 2 CH_3, 2 CH_2); 1.06—1.12 (m, 4 H, 2 CH_2); 1.15—1.21 (m, 4 H, 2 CH_2); 1.26—1.36 (m, 12 H, 6 CH_2); 1.38—1.45 (m, 4 H, 2 CH_2); 1.60—1.66 (m, 4 H, 2 CH_2); 2.26, 2.48 (both s, 6 H each, 4 CH_3 in two pyrazolyls); 3.79—3.82 (m, 4 H, 2 NCH_2); 4.00 (t, 4 H, 2 OCH_2, *J* = 6.5 Hz); 6.23 (s, 2 H, 2 C(4)H in two pyrazolyls); 7.13 (d, 2 H, C(1)H, C(7)H, *J* = 1.9 Hz); 7.17 (d, 4 H, 4 CH in 2 Ar, *J* = 8.5 Hz); 7.45 (d, 2 H, C(4)H, C(10)H, *J* = 8.8 Hz); 7.50 (dd, 2 H, C(3)H, C(9)H, J_1 = 8.8 Hz, J_2 = 1.9 Hz); 7.53 (d, 4 H, 4 CH_{Ar}, *J* = 8.5 Hz); 10.72 (br.s, 2 H, 2 NH). ^{13}C NMR (DMSO-d_6, δ): 12.30, 13.29, 13.71, 13.83, 21.99, 22.05, 25.08, 25.85, 28.33, 28.53, 28.92, 30.76, 30.99, 67.43, 108.55, 108.66, 115.04 (2 C), 115.23, 117.72, 120.38, 122.17, 122.20, 128.26, 128.93, 130.87 (2 C), 132.68, 139.38, 141.39, 150.07, 157.02, 158.64, 160.35.

***N*-Ethyl-5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazol-2-amine (7).** To amine **3** (592 mg, 1 mmol), pyridine (4 mL) and acetyl chloride (235 mg, 3 mmol) was added and the mixture was stirred for 15 min at room temperature. Then, H_2O (50 mL) was added and the mixture was extracted with CH_2Cl_2 (3×15 mL). The extract was concentrated, the solid residue was added to a suspension prepared by adding small portions of $AlCl_3$ (445 mg, 3.33 mmol) to $LiAlH_4$ (380 mg, 10 mmol)) in THF (10 mL) under ice cooling. The orange solution thus prepared was refluxed for 1 h. The unreacted aluminum hydride was decomposed by successively adding methanol (2 mL) and 1 mL 50% aqueous NaOH (all inorganic compounds formed compact granules). The organic phase was decanted and the solvents were removed at a reduced pressure. The bright yellow product was recrystallized from isopropyl alcohol (5 mL), washed with methanol (2×2 mL), and dried at 110 °C. The yield was 440 mg (71%). M.p. 144—145 °C. R_f = 0.72 (with THF as eluent). Found (%): C, 85.17; H, 7.85; N, 6.65. $C_{44}H_{49}N_3$. Calculated (%): C, 85.25; H, 7.97; N, 6.78. ^{1}H NMR (C_6D_6, δ): 0.77—0.86 (m, 10 H, 2 CH_2CH_3); 0.94 (t, 3 H, $NCH_2C\underline{H}_3$, *J* = 7.1 Hz); 0.96—1.03 (m, 4 H, 2 CH_2); 1.09—1.17 (m, 4 H, 2 CH_2); 1.42—1.50 (m, 4 H, 2 CH_2); 2.79 (q, 2 H, $NC\underline{H}_2CH_3$, *J* = 7.1 Hz); 3.72—3.77 (m, 4 H, 2 NCH_2); 6.15 (d, 1 H, C(1)H, *J* = 2.2 Hz); 6.72 (dd, 1 H, C(3)H, J_1 = 8.5 Hz, J_2 = 2.2 Hz); 6.97—7.00 (m, 1 H, CH_{ICZ}); 7.05 (d, 1 H, CH_{ICZ}, *J* = 7.6 Hz); 7.14—7.16 (m, 1 H, CH_{ICZ}); 7.21 (d, 1 H, CH_{ICZ}, *J* = 8.1 Hz); 7.27—7.36 (m, 7 H, 6 CH_{Ph}, 1 CH_{ICZ}); 7.63—7.66 (m, 4 H, 4 CH_{Ph}).

Reaction of compound 7 with DPTz. ***A.*** To DPTz (135 mg, 0.5 mmol) in mesitylene (5 mL), ICZ **7** (310 mg, 0.5 mmol) was added. The reaction mass was refluxed for 13 h, cooled to room temperature, and transferred to a column with silica gel. The mixture was separated by column chromatography with CH_2Cl_2 as eluent.

B. To DPTz (14 mg, 0.05 mmol), compound **7** (31 mg, 0.05 mmol) was added and the reaction mass was ground to a homogeneous mixture, heated until melting (140 °C), and kept at this temperature for 20 min. The mixture of products was analyzed by LC-HRMS.

***N*-[6-(3,5-Dimethylpyrazol-1-yl)-1,2,4,5-tetrazine-3-yl]-*N*-ethyl-5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazol-2-amine (8).** Found: *m/z* 794.4630 $[M + H]^+$. $C_{51}H_{56}N_9^+$. Calculated: $[M + H]^+$ = 794.4653.

3,6-Bis(3,5-dimethylpyrazol-1-yl)pyridazine (9). ^{1}H NMR ($CDCl_3$, δ): 2.31, 2.75 (both s, 6 H each, 4 CH_3 in two pyrazolyls); 6.07 (s, 2 H, 2 C(4)H in two pyrazolyls); 8.22 (s, 2 H, C(4)H, C(5)H in pyridazine). Found: *m/z* 269.1513 $[M + H]^+$. $C_{14}H_{17}N_6^+$. Calculated: $[M + H]^+$ = 269.1509.

The authors express their gratitude to Cand. Sci. (Chem.) A. I. Zvyagina for carrying out X-ray diffraction experiments on facilities at the Center for Collective Use of Physical Methods of Investigation at the A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences.

This work was financially supported by the Ministry of Science and Education of the Russian Federation within the framework of the State Assignment themes (Nos AAAA-A19-119012490006-1, AAAA-A19-119012290116-9, and AAAA-A19-119012290117-6) using facilities at the Center for Collective Use "Spectroscopy and Analysis of Organic Compounds" at I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences. Charge carrier mobility studies were financially supported by the Russian Foundation for Basic Research (Project No. 18-29-23045 mk). Experimental UV photoelectron spectroscopy studies were carried out on facilities at the "Nanochemistry and Nanomaterials" Center for Collective Use, Department of Chemistry, M. V. Lomonosov Moscow State University.

This paper does not contain descriptions of studies on animals or humans.

The authors declare no competing interests.

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Received March 2, 2021;
in revised form April 5, 2021;
accepted April 7, 2021.