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Synthesis of New Polydentate Tweezers Ligands of Amido-Amine Type

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Abstract—A series of new tweezers amido-amine ligands containing pyrrole, bipyrrole, and dipyrrolylmethane fragments were synthesized by reaction of 2-thioxothiazolidin-3-yl derivatives of α-pyrrolecarboxylic acids {5-[1-(5-carboxy-3-methyl-4-phenyl-1*H*-pyrrol-2-yl)-1-methylethyl]-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylic acid, 5-[(5-carboxy-3-methyl-4-phenyl-1*H*-pyrrol-2-yl)phenylmethyl]-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylic acid, 5-(5-carboxy-3-methyl-4-phenyl-1*H*-pyrrol-2-yl)-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylic acid, and 3,4-dimethylpyrrole-2,5-dicarboxylic acid} with *o*-phenylenediamine. All compounds obtained were characterized by elemental analysis, NMR and mass spectra.

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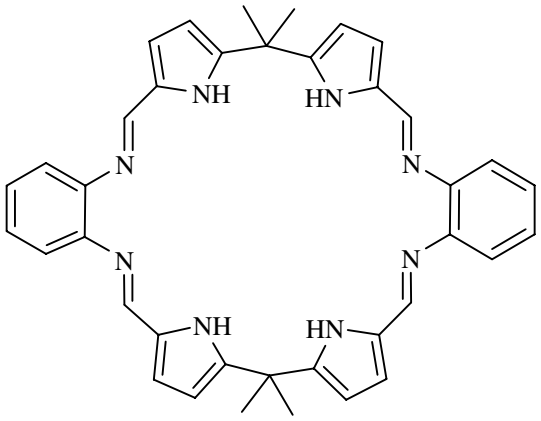
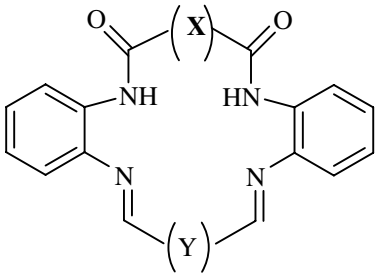
Polydentate ligands containing structural fragments of pyrrole, bipyrrole, and dipyrrolylmethane are very interesting objects for preparation of mono- and binuclear complexes of transition metals [1–3], and also as building blocks for synthesis of hybrid macrocyclic Schiff bases which we have recently shown[4–7] to be capable of selective binding anions and thus behave as highly efficient artificial anion receptors. Among these compounds by now Schiff bases **Ia** were described that were prepared from the corresponding diformyl derivatives of pyrrole by anion-template method [3]. Even more promising for building up artificial anion receptors are amides of appropriate α-carboxylic acids since the amide CONH groups alongside pyrrole NH groups [8, 9] are capable to bind anions by forming with them strong hydrogen bonds.

Amide of this type containing thiophene amd pyridine fragment **Ic** and **Id** we synthesized from the corresponding dicarboxylic acids or their derivatives and two equiv of symmetric diamines [5, 7]. To carry out selective synthesis one amino group of the diamine was sometimes protected, and deprotection was performed in the last stage of the process [4]. The synthesis of compound **Ib** with two or more pyrrole rings is the goal of the present investigation and is a more complex synthetic problem owing to the known acidophobicity of α-pyrrolecarboxylic acids and to their capability to extremely readily decarboxylation in acid media, and also to *ipso*-substitution of the carboxy group in the majority of pyrroles with alkyls at the third and fourth positions of the ring. Introduction of electron-acceptor groups to the pyrrole ring somewhat increases the stability of the α-carboxylic acids and makes it possible to obtain their derivatives. 3,4-Dimethyl-5-ethoxycarbonylpyrrole-2-carboxylic acid and 3,4-diphenylpyrrole-2,5-dicarboxylic acid are sufficiently stable against decarboxylation, and within the last decade a series of their derivatives has been synthesized, in particular amides [9, 10]. Preliminary tests carried out by us showed that dicarboxylic acids from 2,2'-bipyrrole and 2,2'-dipyrrolylmethane with aliphatic substituents in positions *3*, *4* were to such degree thermally unstable and acidophobic that we failed to synthesize any derivatives by the carboxy group. At the same time 3,4-diphenylpyrrole-2,5-dicarboxylic acid is sufficiently stable compound [11] capable even to form acyl chloride by reaction with thionyl chloride. Therefore to raise the stability of initial acids we introduced in the ring a phenyl substituent adjacent to the carboxy group.

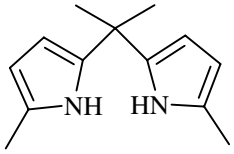
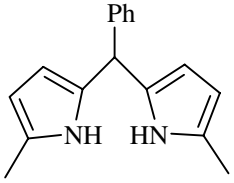
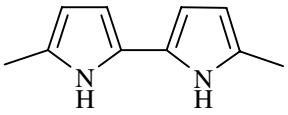
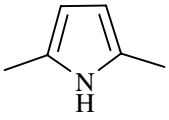
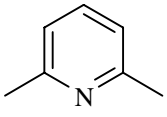
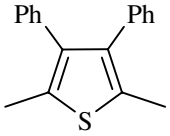
The initial ethyl 4-methyl-3-phenylpyrrole-2-carboxylate (**II**) was easily obtained by Barton–Zard reaction [12]. Applying the known semimicro synthetic procedure [13] we carried out the reaction in THF for 16 h, and then after purification by column chromatography we obtained compound **II** in 54% yield. The modification of the procedure for preparative synthesis (the reaction performed in THF–2-propanol mixture) reduced the

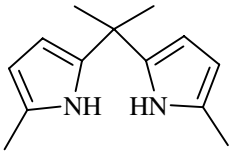
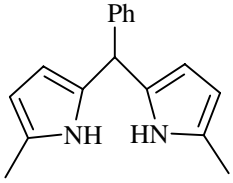
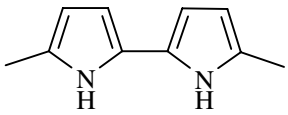
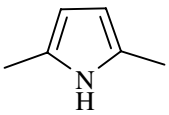


Ia

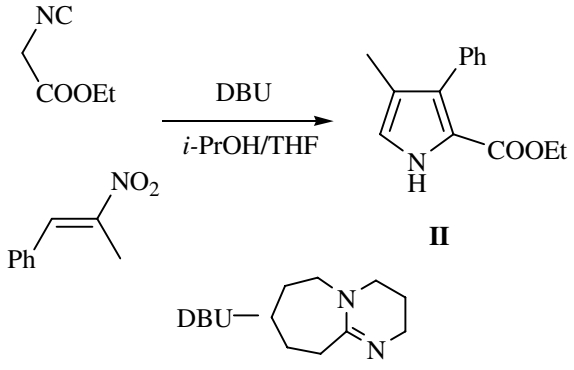


Ib–**Id**

X =  ,  ,  ,  (**b**),  (**c**),  (**d**);

Y =  ,  ,  ,  .

reaction time to 4 h, and after simple recrystallization the pure compound **II** was obtained in 95% yield.

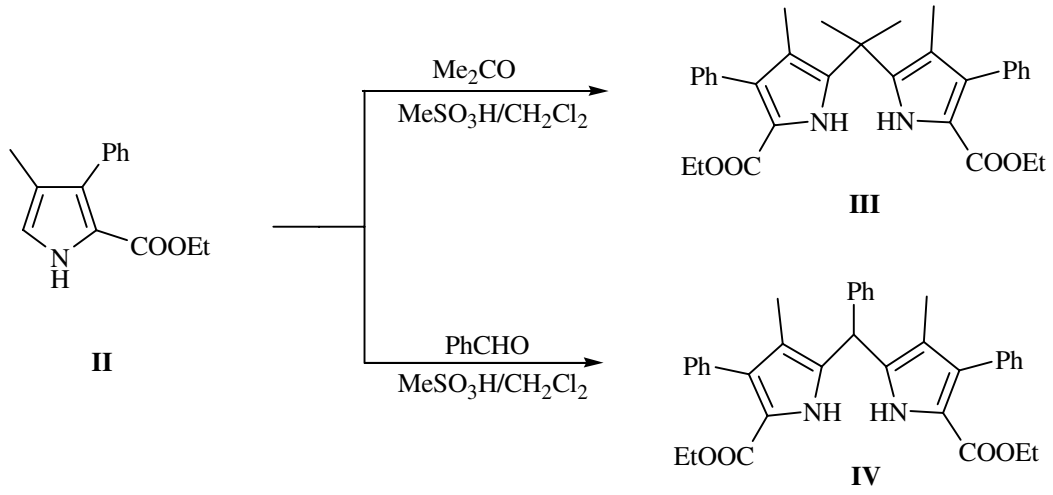


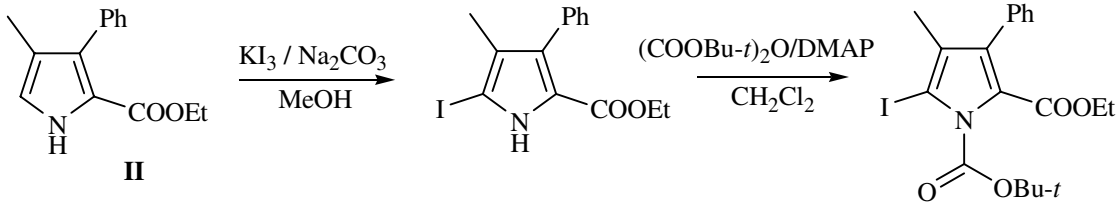
II

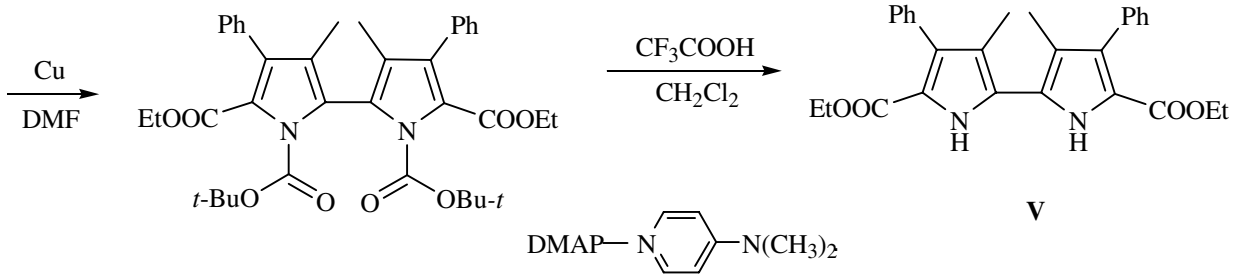
The transformation of ester **II** into the corresponding bispyrrole derivatives was performed by known procedures. The known acid-catalyzed pyrrole reaction with carbonyl compounds (in our case with acetone and benzaldehyde) led to the formation in yields about 70% mono- and bis-*meso*-substituted dipyrrolylmethanes **III** and **IV**. The cross-coupling Ullmann reaction formerly adjusted for pyrroles by Sessler [14] gave in four stages bipyrrole **V**.

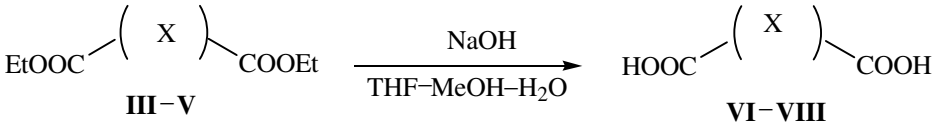
The choice of these three basic structures as objects of the synthesis and further investigation was governed by the fact that the distances between the carboxy groups in these compounds were different and grew in the series **III** < **IV** < **V**. This fact and also their various conformational lability provided a possibility to build up therefrom macrocycles of variable rigidity with different dimensions of inner voids.

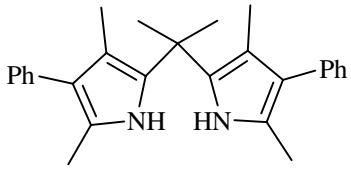
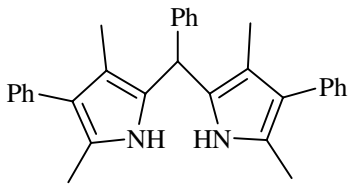
Ethyl esters **III**–**V** are stable compounds melting without decomposition. They all were readily and quantitatively hydrolyzed in a system THF–methanol–water into the corresponding dicarboxylic acids **VI**–**VIII**. Note that ester **IV** unlike compound **III** is capable to be oxidized into the corresponding dipyrrolemethine derivative.

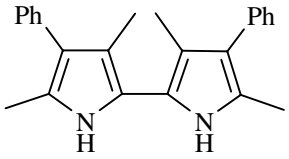


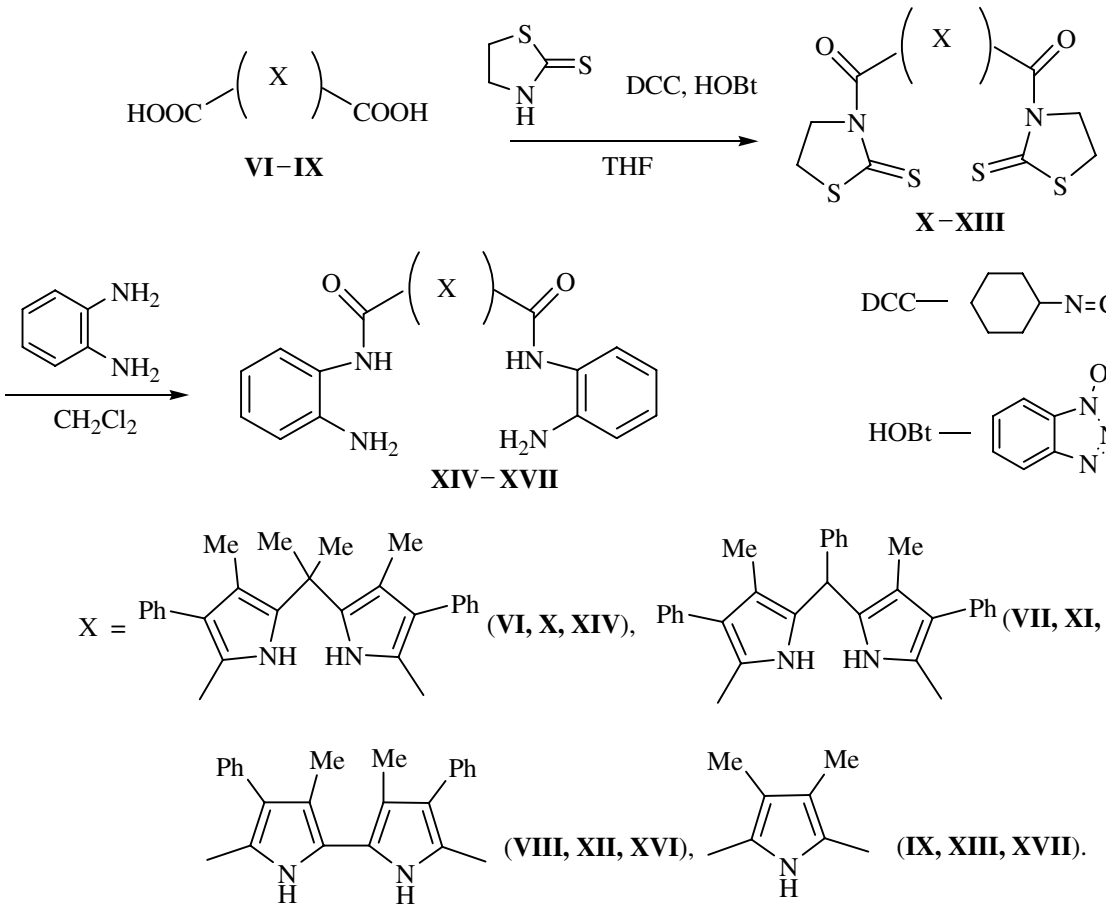






X =  (**III,VI**),  (**IV,VII**),

 (**V,VIII**).



Dicarboxylic acids **VI–VIII** are more stable than their analogs containing only alkyl groups at the pyrrole ring. Still they slowly decompose in solution at storage and in the solid state at heating. We attempted to synthesize their amides through intermediate acyl chlorides which we tried to obtain by reactions with thionyl chloride and oxalyl chloride. The target products were obtained only in reaction with a large excess of aliphatic diamine. The selectivity and yield in these reactions were low, as had been previously found for analogous compounds [15]. We failed to isolate the target diamides with *o*-phenylenediamine both in reactions via acyl chlorides and at a milder activation of the acids by means of dicyclohexylcarbodiimide. In reactions via acyl chlorides formed mainly oligomeric products, and with dicyclohexylcarbodiimide the reaction failed to proceed due to low nucleophilicity (and, consequently, diminished reactivity) of aromatic amines. We succeeded in preventing oligomerization using 2-thioxothiazolan-3-yl departing group, less active than chlorine. This group was already successfully used in preparation of amides from aromatic diamines [16].

2-Thioxothiazolan-3-yl derivatives **X–XIII** of pyrrolecarboxylic acids **VI–VIII**, and also of known 3,4-dimethylpyrrole-2,5-dicarboxylic acid (**IX**) were obtained by treating the acids with 1,3-thiazolane-2-thione in the presence of dicyclohexylcarbodiimide and benzotriazol-1-ol. They were oily substances of low stability, therefore after separation from side products and distilling off the solvent the compounds were without further purification at once brought into reaction with *o*-phenylenediamine.

Diamides **XIV–XVII** were obtained in reactions with a large excess of *o*-phenylenediamine in dichloromethane at room temperature for 5–7 days. They were easily isolated from the reaction mixture by simple filtration (compounds **XVI** and **XVII**), by recrystallization from ethanol after evaporating the solvent (**XIV**), or by column chromatography on silica gel (**XV**). All compounds obtained were characterized by NMR and mass spectra and by elemental analysis. The synthesis of unsymmetrical polypyrrole mactocyles of amido-imine type **Ib** using diamides **XIV–XVII** will be published in next communications.

EXPERIMENTAL

NMR spectra were registered on a spectrometer Bruker AVANCE-400, mass spectra were measured on instruments Finnigan-MAT-SSQ-7000 (GC-MS) and Bruker MALDI-TOF Reflex 3 (MALDI-TOF). Ethyl isocyanoacetate, 1-phenyl-2-nitropropene, and 3,4-dimethyl-1*H*-pyrrole-2,5-dicarboxylic acid were prepared by known procedures [17–19]. DBU, 1,3-thiasolane-2-thion, DCC, benzotriazol-1-ol, and *o*-phenylenediamine purchased from Acros were used without additional purification. Anhydrous THF for reactions was obtained by distillation over sodium ketyl (stable blue color) in the presence of a small quantity of benzophenone. Dichloromethane, 2-propanol, and dimethylformamide for reactions were distilled over calcium hydride. The chromatography was performed using silica gel Merck Kieselgel 60, 40–60 μm.

Ethyl 4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylate (II). To a solution of 8.3 g (51 mmol) of 1-phenyl-2-nitropropene in 60 ml of mixture THF–2-propanol, 3:1 v/v, was added 5 g (44 mmol) ethyl isocyanoacetate and then dropwise at stirring 6 g (45 mmol) of DBU maintaining the temperature of the reaction mixture below 15°C by cooling with a water bath. The reaction mixture was stirred for 3 h more at room temperature (after 1 h a precipitate formed), then the solvent was evaporated in a vacuum at the temperature not exceeding 50°C, to the residue 30 ml of ether and 30 ml of water was added, and stirring was continued till complete dissolution of solids. The organic phase was separated, the water phase was extracted with ether (2×30 ml). The combined organic solutions were washed with 10% HCl (2×30 ml), water, saturated NaCl solution, and dried with sodium sulfate. The solvent was removed in a vacuum, the residue was recrystallized from petroleum ether (bp 40–70°C). Yield 9.5 g (95%), yellowish crystalline substance, mp 63°C (oily substance according to [13]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.13 t (3H, *J* 7.5 Hz), 2.01 s (3H), 4.15 q (2H, *J* 7.5 Hz), 6.45 d (1H, *J* 1.6 Hz), 7.51–7.22 m (5H), 9.23 br (1H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 10.76, 14.23, 60.15, 119.82, 119.91, 124.40, 127.25, 127.91, 130.45, 132.41, 134.23, 161.23. Mass spectrum, *m/z* (I_{rel}, %): 229.1 (100) $[M]^+$. Found, %: C 73.07; H 6.60; N 6.08. $C_{14}H_{15}NO_2$. Calculated, %: C 73.34; H 6.59; N 6.11.

Ethyl 5-iodo-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylate. This synthesis should be protected from bright light. To a solution of 20.6 g (0.92 mmol) of compound **II** in 200 ml of methanol was added a solution of 22 g of sodium hydrogen carbonate in 200 ml of water. To a suspension thus obtained was added within 2 h at 50°C while stirring a solution of 23 g of iodine and 33.5 g of potassium iodide in 150 ml of a mixture methanol–water, 2:1 v/v. The reaction mixture was stirred for 2 h more at this temperature, then it was poured into 1 l of water with ice. Excess iodine was neutralized with sodium thiosulfate till decoloration of the solution over precipitate. The precipitate was filtered off and dried in a vacuum desiccator over calcium chloride for 24 h. Yield 30.3 g (95%). The reaction product was sufficiently pure to be used in the next stage of the synthesis. mp 83°C (hexane–ether, 3:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.12 t (3H, *J* 7.5 Hz), 2.09 s (3H), 4.18 q (2H, *J* 7.5 Hz), 7.39 m (5H), 9.05 br (1H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 10.89, 14.16, 60.51, 119.43, 119.95, 124.58, 127.18, 127.71, 130.62, 132.27, 134.49, 161.30. Mass spectrum, *m/z* (I_{rel}, %): 355.0 (100) $[M]^+$. Found, %: C 47.63; H 4.06; N 3.98. $C_{14}H_{14}INO_2$. Calculated, %: C 47.34; H 3.97; N 3.94.

Dipyrrolylmethanes III and IV. To a solution of 40 mmol of compound **II** in 50 ml of anhydrous dichloromethane under an argon atmosphere was added at stirring 25 mmol of acetone (**III**) or benzaldehyde (**IV**) and 1 ml of methanesulfonic acid, and then the reaction mixture was stirred for 24 h. To the mixture 30 ml of 10% solution of NaOH was added, and the stirring was continued for another 30 min (the color changed from dark red to orange). On separating the organic layer the reaction products were additionally extracted from the water phase with dichloromethane (2×20 ml), the combined organic solvents were washed with water, saturated NaCl solution, and dried with sodium sulfate. On distilling off the solvent the residue was ground with ethanol, filtered off, and additionally washed with anhydrous ethanol till the filtrate became colorless. Reaction product was colorless fine crystalline substance.

Ethyl 5-[1-(5-ethoxycarbonyl-3-methyl-4-phenyl-1*H*-pyrrol-2-yl)-1-methylethyl]-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylate (III). Yield 71%, mp 195°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.11 t (6H, *J* 7.5 Hz), 1.56 s (6H), 1.79 C (6H), 4.13 q (2H, *J* 7.5 Hz), 7.35 m (10H), 8.89 br (1H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 8.23, 14.16, 32.94, 42.44, 62.92, 103.36, 116.85, 127.54, 128.81, 129.37, 132.45, 134.54, 136.37, 160.15. Mass spectrum, *m/z* (I_{rel}, %): 498.25 (100) $[M]^+$, 483 (73) $[M - CH_3]^+$. Found, %: C 74.53; H 6.96; N 5.76. $C_{31}H_{34}N_2O_4$. Calculated, %: C 74.67; H 6.87; N 5.62.

Ethyl 5-[(5-ethoxycarbonyl-3-methyl-4-phenyl-1*H*-pyrrol-2-yl)phenylmethyl]-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylate (IV). Yield 68%, mp 210°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.06 t (6H), 1.82 s (6H), 4.07 q (4H), 5.66 s (1H), 7.32 m (15H), 8.82 br (2H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 9.46, 13.92, 41.23, 59.94, 117.67, 117.82, 126.69, 127.20, 127.35, 127.67, 128.32, 129.20, 130.39, 131.67, 132.22, 134.68, 138.67, 161.20. Mass spectrum, *m/z* (I_{rel}, %): 546.2 (100) $[M]^+$. Found, %: C 76.83; H 6.11; N 4.95. $C_{35}H_{34}N_2O_4$. Calculated, %: C 76.90; H 6.27; N 5.12.

Ethyl 5-(3-methyl-4-phenyl-5-ethoxycarbonyl-1*H*-pyrrol-2-yl)-4-methyl-3-phenyl-*1H*-pyrrole-2-carboxylate (V) was obtained by procedure [9]. To 22 g (0.062 mol) of ethyl-5-iodo-4-methyl-3-phenylpyrrole-2-carboxylate and 1 g of DMAP in 250 ml of anhydrous dichloromethane was added by portions 18 g of di-*tert*-butyl dicarbonate. The mixture was stirred for 3 h till the end of gas liberation. The transparent solution obtained was passed through a bed of silica gel (80 × 40 mm) and evaporated in a vacuum. The oily substance obtained without further purification was dissolved in 120 ml of DMF under an argon atmosphere, and at stirring 25 g of copper powder was added. The reaction mixture was heated to 110°C and stirred for 30 h at this temperature. Then it was cooled and filtered through a bed of silica gel (50 × 40 mm) to remove copper compounds, the elution with chloriform (about 300 ml) was continued till colorless solution. The eluate was washed with 10% solutions of HCl (3 × 100 ml) and $Na_2S_2O_3$ (3 × 100 ml), with saturated solutions of $NaHCO_3$ (100 ml) and NaCl (100 ml), dried with sodium sulfate, and the solvent was removed in a vacuum. The oily residue without additional purification was dissolved in 150 ml of dichloromethane, and 50 ml of trifluoroacetic acid was added to the solution. The mixture was stirred till the end of gas liberation (2–3 h), then 100 ml of water was added. The organic phase was separated and trice washed with 10% solution of NaOH and with saturated NaCl solution (adding dichloromethane in case organic substance precipitated), then the solution was dried with sodium sulfate. On removing the solvent in a vacuum and recrystallization of the residue from ethanol we obtained 7.5 g of compound **V** as a grayish powder. Yield 54% (overall), mp 235°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.12 t (6H, *J* 7.5 Hz), 2.09 s (6H), 4.18 q (4H, *J* 7.5 Hz), 7.39 m (10H), 9.05 br (2H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 10.96, 14.28, 60.46, 119.37, 119.80, 124.63, 127.20, 127.80, 130.55, 132.33, 134.54, 161.20. Mass spectrum, *m/z* (I_{rel}, %): 456.20 (100) $[M]^+$.Found, %: C 73.61; H 5.91; N 5.98. $C_{28}H_{28}N_2O_4$. Calculated, %: C 73.66; H 6.18; N 6.14.

Acids VI–VIII. In 20 ml of THF was dissolved 10 mmol of ester **III–V**, and a solution of 2 g (50 mmol) of NaOH in 10 ml of water was added. To the two-phase system obtained methanol (about 20–30 ml) was added at stirring till the system turned homogeneous, and the mixture was boiled for 5 h. On cooling the organic solvents were distilled off in a vacuum while replacing them with warm distilled water. The crystalline precipitate of the dicarboxylic acid sodium salt was filtered off and washed with warm water, then it was dissolved in 70–100 ml of methanol (at heating when necessary), filtered, and cooled to –10°C. The cold solution was quickly neutralized with concn. HCl till pH 1.0–1.5, the separated dicarboxylic acid was filtered off and washed with cold (–10°C) methanol. On drying in a vacuum the product obtained was a pure dicarboxylic acid.

5-[1-(5-Carboxy-3-methyl-4-phenyl-1*H*-pyrrol-2-yl)-1-methylethyl]-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylic acid (VI). Yield 96%, mp 180°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.39 s (6H), 1.76 s (6H), 7.35 m (10H), 10.47 s (2H), 11.8 br (2H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 8.31, 33.03, 103.43, 116.91, 127.42, 128.76, 129.37, 132.46, 134.54, 136.32, 159.55. Mass spectrum, *m/z*: 466 $[M + Na + H]^+$, 488 $[M + 2Na – 2H]^+$, 510 $[M + 3Na – 3H]^+$, 442 $[M]^–$. Found, %: C 73.13; H 5.97; N 6.08. $C_{27}H_{26}N_2O_4$. Calculated, %: C 73.28; H 5.92; N 6.33.

5-[(5-Carboxy-3-methyl-4-phenyl-1*H*-pyrrol-2-yl)phenylmethyl]-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylic acid (VII). Yield 89%, mp 180°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.95 s (6H), 5.82 s (1H), 7.28 m (15H), 11.55 s (2H), 11.90 br (2H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 9.95, 38.48, 117.27, 118.63, 126.63, 126.82, 127.77, 128.25, 128.66, 128.73, 130.24, 130.80, 132.86, 135.71, 141.50, 162.31. Mass spectrum, *m/z*: 514 $[M + Na + H]^+$, 490 $[M]^+$, 446 $[M – CO_2]^+$, 402 $[M – 2CO_2]^+$, 490 $[M]^–$, 512 $[M + Na – H]^–$. Found, %: C 76.25; H 5.22; N 5.80. $C_{31}H_{26}N_2O_4$. Calculated, %: C 75.90; H 5.34; N 5.71.

5-(5-Carboxy-3-methyl-4-phenyl-1*H*-pyrrol-2-yl)-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylic acid (VIII). Yield 93%, mp 220°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.88 s (6H), 7.31 m (10H), 11.51 s (2H), 11.98 br (2H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 10.84, 118.45, 118.89, 124.72, 126.23, 126.87, 127.39, 128.35, 130.30, 135.19, 161.73. Mass spectrum,

m/z: 400 $[M]^+$, 356 $[M - CO_2]^+$, 400 $[M]^-$, 355 $[M - CO_2 - H]^-$. Found, %: C 72.36; H 4.91; N 6.85. $C_{24}H_{20}N_2O_4$. Calculated, %: C 71.99; H 5.03; N 7.00.

Amides XIV–XVII. A solution or suspension of 10 mmol of dicarboxylic acid in 70 ml of anhydrous THF under argon was cooled to–5°C, and then 4.53 g (22 mmol) of dicyclohexylcarbodiimide was added, and after that 2.97 g (22 mmol) of benzotriazol-1-ol, and the mixture was stirred for 30–40 min at room temperature (when necessary the reaction mixture was heated to complete dissolution of the acid). To a solution thus obtained 2.62 g (22 mmol) of 1,3-thiazolane-2-thione was added, and the mixture was stirred for 48 h. The separated precipitate was filtered off and washed with THF. The filtrate was evaporated to dryness in a vacuum, the residue was dissolved in anhydrous dichloromethane, and filtered. To the transparent solution 7.13 g (66 mmol) of *o*-phenylenediamine was added, and the stirring continued for 5–7 days. The isolation of the reaction product was adjusted to each special case.

2-Aminophenylamide of 5-{1-[5-(2-aminophenylcarboxamido)-3-methyl-4-phenyl-1*H*-pyrrol-2-yl]-1-methylethyl}-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylic acid (XIV). The solvent was distilled off in a vacuum, the residue was twice recrystallized from ethanol. Yield 42%, light-yellow substance, mp 152°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.52 s (6H), 1.87 s (6H), 4.55 br (4H), 6.47 d.t (2H, J_1 8, J_2 1.6 Hz), 6.65 d.d (2H, J_1 8, J_2 1.6 Hz), 6.90 d.t (2H, J_1 8, J_2 1.6 Hz), 7.17 d.d (2H, J_1 8, J_2 1.6 Hz), 7.30 m (2H), 7.42 m (8H), 8.05 s (2H), 10.57 s (2H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 10.01, 28.17, 36.58, 115.01, 115.17, 116.57, 117.01, 119.76, 124.06, 125.24, 126.00, 127.21, 128.61, 129.36, 130.86. 135.83, 137.25, 142.16, 159.46. Mass spectrum, *m/z*: 645 $[M + Na]^+$. Found, %: C 74.93; H 6.09; N 13.47. $C_{39}H_{38}N_6O_2$. Calculated, %: C 75.22; H 6.15; N 13.49.

2-Aminophenylamide of 5-{[5-(2-aminophenylcarboxamido)-3-methyl-4-phenyl-1*H*-pyrrol-2-yl]phenylmethyl}-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylic acid (XV). The solvent was distilled off in a vacuum, the reaction product was isolated by column chromatography on silica gel, eluent dichloromethane–methanol, 9:1 v/v. Yield 45%, R_f 0.35–0.40, mp 150°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.98 s (6H), 4.48 br (4H), 5.87 s (1H), 6.52 d.t (2H, J_1 8, J_2 1.6 Hz), 6.65 d.d (2H, J_1 8, J_2 1.6 Hz), 6.83 d.t (2H, J_1 8, J_2 1.6 Hz), 7.20 d.d (2H, J_1 8, J_2 1.6 Hz), 7.22–7.46 m (15H), 10.09 s (2H), 11.55 s (2H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 9.81, 33.30, 116.53, 116.66, 122.47, 124.00, 124.71, 125.86, 126.45, 126.85, 127.67, 127.85, 128.27, 128.37, 128.69, 129.08, 130.68, 130.87, 131.73, 135.47, 141.70, 159.68. Mass spectrum, *m/z*: 693 $[M + Na]^+$. Found, %: C 76.65; H 5.96; N 12.39. $C_{43}H_{38}N_6O_2$. Calculated, %: C 76.99; H 5.71; N 12.53.

2-Aminophenylamide of 5-[5-(2-aminophenylcarboxamido)-3-methyl-4-phenyl-1*H*-pyrrol-2-yl]-4-methyl-3-phenyl-1*H*-pyrrole-2-carboxylic acid (XVI). The colorless precipitate was filtered off, washed with dichloromethane, ethanol, and ether, and dried in a vacuum. Yield 38%, mp 220°C (decomp.) ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.97 s (6H), 4.70 br (4H), 6.51 d.t (2H, J_1 8, J_2 1.6 Hz), 6.68 d.d (2H, J_1 8, J_2 1.6 Hz), 6.82 d.t (2H, J_1 8, J_2 1.6 Hz), 7.21 d.d (2H, J_1 8, J_2 1.6 Hz), 7.32 m (2H), 7.44 m (8H), 8.09 s (2H), 11.59 s (2H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm:11.24, 116.38, 116.78, 118.00, 123.17, 123.82, 125.30, 126.03, 127.18, 128.00, 128.61, 130.73, 135.47, 142.14, 159.55. Mass spectrum, *m/z*: 580 $[M]^+$, 603 $[M + Na]^+$. Found, %: C 74.21; H 5.48; N 14.27. $C_{36}H_{32}N_6O_2$. Calculated, %: C 74.46; H 5.55; N 14.47.

N^2,N^5-Bis(2-aminophenyl)amide of 3,4-dimethylpyrrole-2,5-dicarboxylic acid (XVII). Yellow precipitate was filtered off, washed with dichloromethane, ethanol, and ether, and dried in a vacuum.Yield 34%, mp 250°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.26 s (6H), 4.93 br (4H), 6.59 d.t (2H, J_1 8, J_2 1.6 Hz), 6.78 d.d (2H, J_1 8, J_2 1.6 Hz), 6.95 d.t (2H, J_1 8, J_2 1.6 Hz), 7.26 d.d (2H, J_1 8 , J_2 1.6 Hz), 9.04 s (2H), 11.63 s (2H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 10.52, 116.56, 116.81, 123.76, 124.43, 126.37, 142.77, 160.04. Mass spectrum, *m/z*: 363 $[M]^+$. Found, %: C 66.04; H 5.82; N 19.09. $C_{20}H_{21}N_5O_2$. Calculated, %: C 66.10; H 5.82; N 19.27.

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