

Synthesis of Monomeric and Oligomeric 1,1'-Methylenebis-(1*H*-pyrazoles) Containing Ethynyl Fragments

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Abstract—1,1'-Methylenebis(1*H*-pyrazole) and 1,1'-methylenebis(3,5-dimethyl-1*H*-pyrazole) reacted with iodine in the presence of iodic acid to give the corresponding 4,4'-diiodo derivatives. Polycondensation of the latter with *p*-diethynylbenzene led to the formation of oligomeric compounds. 1,1'-Methylenebis(4-iodo-1*H*-pyrazoles) were converted into 4,4'-diethynyl derivatives by the Sonogashira and reverse Favorskii reactions, and their oxidative polycondensation in the presence of copper(I) chloride in pyridine also gave oligomeric products with a molecular weight exceeding 9000.

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Bis(pyrazol-1-yl)alkanes are known as neutral bidentate ligands whose complexing properties may be varied over a wide range via introduction of various substituents into the pyrazole rings. Therefore, such ligands attract interest of many researchers. Up to now, coordination compounds of bis(pyrazol-1-yl)alkanes with most transition metals and a number of main group elements were synthesized [1]. Taking into account that bis(pyrazol-1-yl)alkanes strongly tend to form complexes, we believed it reasonable to incorporate their molecules into polymeric chains with a view to obtain chelating macroligands and macromolecular chelates. High-molecular compounds of this type are used as highly efficient and selective sorbents for metal ions, as well as in sensor systems and in the preparation of immobilized catalysts and semiconducting materials [2].

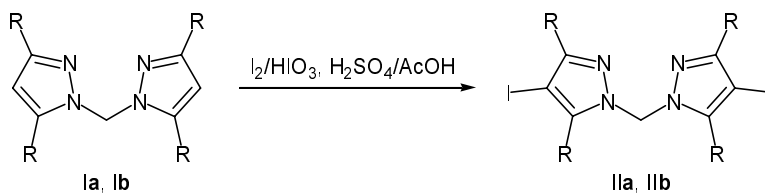
To introduce 1,1'-methylenebis(1*H*-pyrazole) frag-

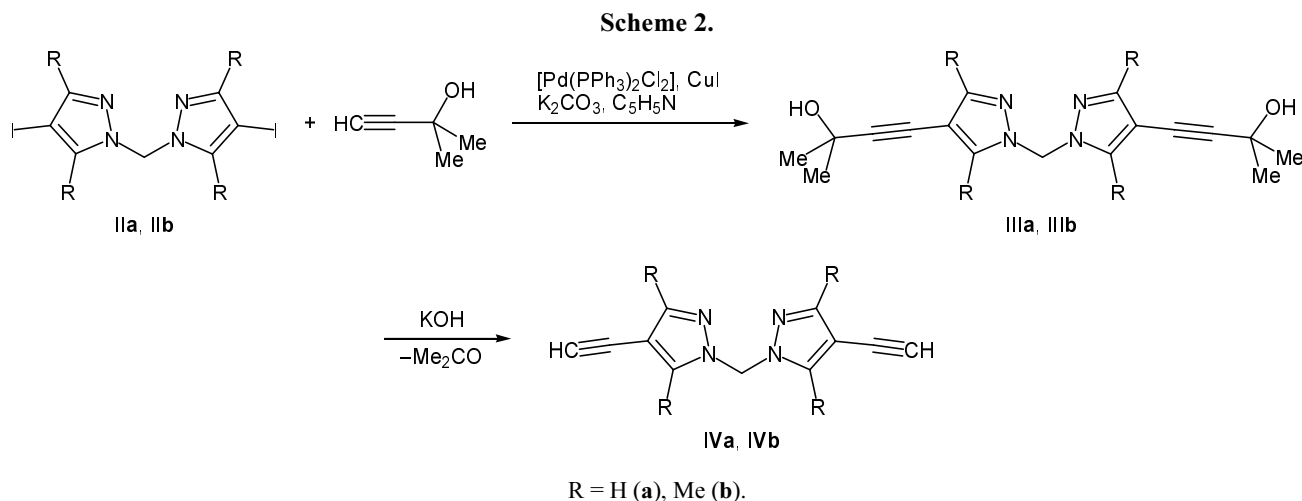
ments into a polymeric chain, the corresponding monomer should contain groups capable of participating in polymerization or polycondensation. Iodine atoms are quite reactive substituents which may be replaced by various functional groups [3], in particular by ethynyl groups under the Sonogashira conditions [4]. Terminal diethynyl derivatives of aromatic compounds are fairly reactive in polycondensations with dihaloarenes; the resulting polymeric compounds [5] are used in the manufacture of sensors, organic light-emitting diodes, and “molecular wires” for nanotechnology [6]. Diethynylarenes are also capable of undergoing oxidative polycondensation catalyzed by copper(I) halides [7].

In the present article we describe the synthesis of 4,4'-diiodo and 4,4'-diethynyl derivatives of 1,1'-methylenebis(1*H*-pyrazole) (**Ia**) and 1,1'-methylenebis(3,5-dimethyl-1*H*-pyrazole) (**Ib**), as well of a number of oligomeric compounds based thereon.

Oxidative iodination of compounds **Ia** and **Ib** was effected with the system I₂–HIO₃–H₂SO₄ in acetic acid

Scheme 1.



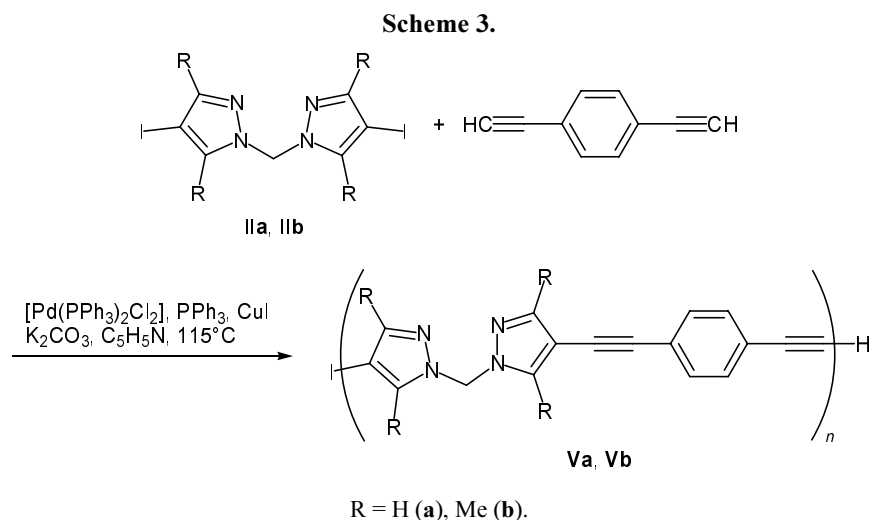


(Scheme 1). This procedure was successfully applied previously in the synthesis of a large number of iodo-substituted *N*-alkylpyrazoles [8]. Compound **Ib** readily reacted with 2 equiv of I_2 - HIO_3 at room temperature to give 94% of diiodo derivative **IIb** in 30 min. The iodination of compound **Ia** having no electron-donor methyl groups required elevated temperature (70°C); nevertheless, the reaction occurred in a regioselective fashion at position 4 of the pyrazole ring with formation of diiodo derivative **IIa** as the only product (yield 98%).

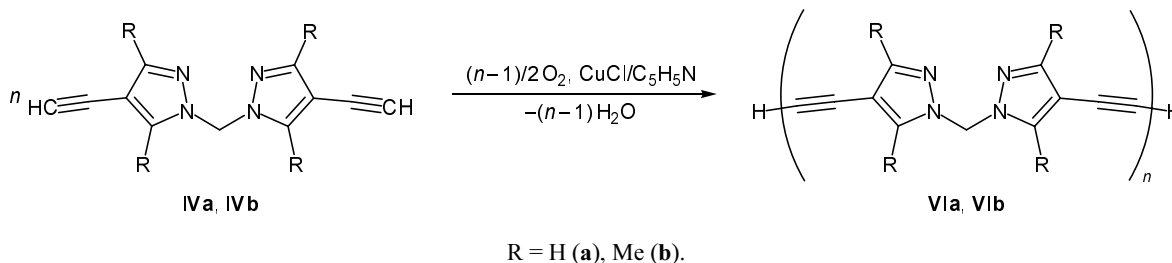
Compounds **IIa** and **IIb** were treated with 2-methylbut-3-yn-2-ol in the presence of $[Pd(PPh_3)_2Cl_2]$ in pyridine (Scheme 2). Analogous ethynylation conditions were reported in [9], and the procedure was similar to that described in [4] for the synthesis of aryl-acetylenes. Cross coupling of diiodo derivatives **IIa** and **IIb** with 2-methylbut-3-yn-2-ol at 100°C occurred at a fairly high rate and gave the corresponding ac-

etylenic alcohols **IIIa** and **IIIb** in a high yield (78%). Alcohols **IIIa** and **IIIb** were converted into terminal acetylenic compounds **IVa** and **IVb** by the retro-Favorskii reaction [10], i.e. via elimination of acetone molecule by the action of KOH in toluene at 110°C (Scheme 2). The reaction was not accompanied by side processes, and the yields of **IVa** and **IVb** were nearly quantitative (92 and 94%, respectively).

By condensation of diiodo derivatives **IIa** and **IIb** with *p*-diethynylbenzene in the presence of 1.5 mol % of $[Pd(PPh_3)_2Cl_2]$ and 3 mol % of CuI in pyridine [5] (Scheme 3) we obtained yellow oligomeric products **Va** and **Vb**. Oligomer **Vb** is soluble in pyridine, chloroform, and dioxane, whereas compound **Va** is insoluble in the above solvents but is sparingly soluble in DMSO. The number-average molecular weights of oligomers **Va** and **Vb** were determined by analysis for iodine. The low degree of polymerization ($\bar{n} = 3$, $\bar{M}_n = 940$ for oligomer **Va** and $\bar{n} = 2$, $\bar{M}_n = 780$ for **Vb**)



Scheme 4.



may be rationalized by the low solubility of these compounds which separate from the solution even at low \bar{n} values. We isolated two fractions of oligomer **Va**: the first of these (fraction 1) was insoluble in pyridine, and it precipitated during the polycondensation process ($\bar{n} = 3$), and the second (fraction 2) was soluble in pyridine on heating ($\bar{n} \approx 1$, according to the NMR data).

Terminal acetylenes **IVa** and **IVb** were brought into oxidative polycondensation according to Hay, which is promoted by oxygen in pyridine in the presence of CuCl [7] (Scheme 4). This reaction usually requires a catalytic amount of copper(I) chloride; however, the polycondensation of compound **IVb** in the presence of 66 mol % of CuCl gave oligomer **VIb** in a poor yield. According to the TLC data, the initial monomer was consumed completely even in 1 h after the reaction started, but the yield of **VIb** was only 14%. Presumably, compound **IVb** with copper(I) chloride forms a strong complex, thus inhibiting the catalytic reaction. By raising the amount of the catalyst and increasing the reaction time we succeeded in obtaining the polycondensation product in 70–86% yield (see table).

The homopolycondensation products are soluble in pyridine and chloroform and sparingly soluble in ethanol and DMSO; they do not melt below 250°C but decompose on heating above that temperature. The ^1H NMR spectra of all oligomers **Va**, **Vb**, **VIa**, and

VIb are characterized by the presence of sets of broadened signals in the same regions as in the spectra of the corresponding monomeric compounds. Absorption bands typical of stretching vibrations of triple carbon–carbon bonds and those belonging to pyrazole ring vibrations were observed in the IR spectra of **Va**, **Vb**, **VIa**, and **VIb**.

The degrees of polymerization and number-average molecular masses of oligomers **VIa** and **VIb** (see table) were determined from the intensity ratios of signals in the ^1H NMR spectra from protons in the terminal groups and other groups constituting the monomer unit. The spectra of samples of **VIb** obtained under different conditions contained a signal at δ 2.38 ppm due to terminal acetylenic protons. With rise in the reaction temperature, the amount of the catalyst being constant, the intensity of the signal at δ 2.38 ppm decreased, and no such signal was observed in the spectrum of a sample obtained at 60°C. These data indicate that the degree of polymerization increases as the polycondensation temperature rises. Probably, this is the result of increase in the solubility of the polycondensation products, which favors prolonged residence of macromolecules in the reaction zone and hence their growth. The intensity of the $\equiv\text{CH}$ signal (δ 2.38 ppm) in the spectrum of oligomer **VIb** obtained at 20°C at a low catalyst concentration was smaller than in the

Oxidative polycondensation of terminal acetylenes **IVa** and **IVb**

Initial compound	CuCl, mol/mol of monomer	Temperature, °C	Reaction time, h	Yield of oligomer, %	\bar{n} (\bar{M}_n)
IVa	2.10	20	4	68	8 (1550)
IVa	2.10	60	4	70	^a
IVb	0.67	20	1	14	–
IVb	0.67	20	4	70	$\bar{n} > 36$
IVb	2.10	20	4	86	18 (4500)
IVb	2.10	40	4	81	36 (9000)
IVb	2.10	60	4	70	$\bar{n} > 36$

^a The degree of polymerization was not determined because of the poor solubility of the product.

spectrum of a sample of **VIb** isolated under similar conditions, but in the presence of a larger amount of the catalyst. Presumably, increased concentration of the catalyst in the reaction mixture ensures larger number of chain initiation and growth acts per unit time, i.e., a larger number of oligomer molecules are formed but they have lower average molecular mass.

We succeeded in determining the degree of polymerization of oligomer **VIa** only for a sample obtained at 20°C ($\bar{n} = 8$, $M_n = 1550$). The product obtained at higher temperature was insufficiently soluble to record its ^1H NMR spectrum. However, we presume that the poorly soluble oligomer is characterized by a higher degree of polymerization ($\bar{n} > 8$). Decrease in the yield of **VIb** with rise in temperature may be attributed to side processes including oxidation of the initial monomer and polycondensation products with oxygen at elevated temperature.

EXPERIMENTAL

The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates. The IR spectra were measured in KBr on a Specord instrument. The NMR spectra were recorded on Bruker AV-300 and Bruker DRX-500 (**Vb**) spectrometers. Signals from the pyrazole rings in the NMR spectra were assigned according to [11].

Initial 1,1'-methylenebis(1H-pyrazoles) **Ia** and **Ib** were synthesized according to the procedure described in [12]. Toluene for the retro-Favorskii reaction was heated for 3 h over metallic sodium under reflux and was then distilled over metallic sodium under atmospheric pressure, a fraction boiling at 110.6°C being collected. Potassium hydroxide was fused in a muffle furnace and heated for 4 h at 600°C. The other reagents were commercial products and were used without additional purification.

1,1'-Methylenebis(4-iodo-1H-pyrazole) (IIa). To a suspension of 3.5 g (23.6 mmol) of compound **Ia**, 4.8 g (18.9 mmol) of finely powdered iodine, and 1.65 g (9.4 mmol) of iodic acid in 30 ml of acetic acid we added 3 ml of 30% sulfuric acid, and the mixture was stirred for 15 min at 70°C until the iodine color disappeared. The mixture was poured into 250 ml of water, and the precipitate was filtered off, washed with water, and dried. The crude product, 9.25 g (98%) (colorless solid) was recrystallized from benzene-hexane (4:1). Yield 8.03 g (85%), colorless crystals, mp 165–165.5°C. IR spectrum, ν , cm^{-1} : 1520, 1395

(pyrazole ring [13]). ^1H NMR spectrum (CDCl_3), δ , ppm: 6.15 s (2H, CH_2), 7.49 s (2H, 3-H), 7.62 s (2H, 5-H). Found, %: C 21.47; H 1.93; I 62.55; N 13.99. $\text{C}_7\text{H}_6\text{I}_2\text{N}_4$. Calculated, %: C 21.02; H 1.51; I 63.46; N 14.01.

1,1-Methylenebis(4-iodo-3,5-dimethyl-1H-pyrazole) (IIb). A suspension of 4.08 g (20 mmol) of compound **Ib**, 4.06 g (16 mmol) of finely powdered iodine, and 1.41 g (8 mmol) of iodic acid in a mixture of 50 ml of acetic acid and 5 ml of 30% sulfuric acid was stirred for 30 min at 20°C until the iodine color disappeared. The mixture was poured into water, and the precipitate was filtered off, washed with water, and dried. Yield 8.55 g (94%), colorless crystals, mp 183–184°C (from ethanol). IR spectrum, ν , cm^{-1} : 1525, 1460, 1370 (pyrazole ring). ^1H NMR spectrum (CDCl_3), δ , ppm: 2.12 s (6H, 3- CH_3), 2.40 s (6H, 5- CH_3), 6.08 s (2H, CH_2). Found, %: C 29.34; H 3.04; N 12.08. $\text{C}_{11}\text{H}_{14}\text{I}_2\text{N}_4$. Calculated, %: C 29.27; H 3.09; N 12.28.

4,4'-[1,1'-Methylenebis(1H-pyrazole-1,4-diyl)]bis(2-methylbut-3-yn-2-ol) (IIIa). A mixture of 2 g (5 mmol) of compound **IIa**, 1.26 g (15 mmol) of 2-methylbut-3-yn-2-ol, 2.7 g (20 mmol) of K_2CO_3 , and 0.143 g (15 mol %) of CuI in 40 ml of pyridine was purged with argon, 0.105 g (3 mol %) of $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ was added, and the mixture was stirred for 6 h at 100°C under argon, diluted with 150 ml of chloroform, and filtered from inorganic salts. The filtrate was washed with 10% aqueous ammonia (6 × 50 ml) until the aqueous layer no longer turned blue and with water (2 × 50 ml) and dried over sodium sulfate. The solvent was removed, and the solid residue was recrystallized from toluene. Yield 1.21 g (78%), colorless crystals, mp 158–159°C (from ethanol). IR spectrum, ν , cm^{-1} : 3320 (O–H); 2220 ($\text{C}\equiv\text{C}$); 1560, 1450, 1370 (pyrazole ring). ^1H NMR spectrum (acetone- d_6), δ , ppm: 1.49 s (12H, CH_3), 3.90 s (2H, OH), 6.39 s (2H, CH_2), 7.52 s (2H, 3-H), 8.03 s (2H, 5-H). ^{13}C NMR spectrum (acetone- d_6), δ_{C} , ppm: 32.1 [$\text{C}(\text{CH}_3)_2$], 65.0 (CH_2), 65.8 [$\text{C}(\text{CH}_3)_2$], 72.5 (4- $\text{C}\equiv\text{C}$), 97.7 (4- $\text{C}\equiv\text{C}$), 104.9 (C^4), 134.0 (C^5), 143.3 (C^3). Found, %: C 65.35; H 6.52; N 18.38. $\text{C}_{17}\text{H}_{20}\text{N}_4\text{O}_2$. Calculated, %: C 65.37; H 6.45; N 17.94.

4,4'-[1,1'-Methylenebis(3,5-dimethyl-1H-pyrazole-1,4-diyl)]bis(2-methylbut-3-yn-2-ol) (IIIb) was synthesized in a similar way from 3.65 g (8 mmol) of diiodo derivative **IIb** and 2.02 g (24 mmol) of 2-methylbut-3-yn-2-ol using 4.42 g (32 mmol) of K_2CO_3 , 0.229 g (15 mol %) of CuI, and 0.168 g (3 mol %) of $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$. Yield 2.32 g (78%),

colorless crystals, mp 168–169°C (from ethanol). IR spectrum, ν , cm^{-1} : 3310 (O–H); 2229 (C≡C); 1567, 1486, 1384 (pyrazole ring). ^1H NMR spectrum (C_6D_6), δ , ppm: 1.64 s [12H, C(CH₃)₂], 2.34 s (6H, 3-CH₃), 2.44 s (6H, 5-CH₃), 3.10 s (2H, OH), 5.64 s (2H, CH₂). ^{13}C NMR spectrum (C_6D_6), δ_{C} , ppm: 10.7 (5-CH₃), 12.7 (3-CH₃), 32.3 [C(CH₃)₂], 60.3 [C(CH₃)₂], 65.5 (CH₂), 73.9 (4-C≡C), 99.3 (4-C≡C), 103.5 (C⁴), 143.4 (C⁵), 150.8 (C³). Found, %: C 68.76; H 7.98; N 14.97. C₂₁H₂₈N₄O₂. Calculated, %: C 68.45; H 7.66; N 15.21.

1,1'-Methylenebis(4-ethynyl-1H-pyrazole) (IVa).

A mixture of 0.624 g (2.0 mmol) of compound **IIIa** and 0.170 g (25 wt %) of KOH in 20 ml of anhydrous toluene was heated for 10 h under reflux. The mixture was filtered, and the solvent was removed from the filtrate under reduced pressure to isolate 0.361 g (92%) of compound **IVa** as colorless crystals with mp 194–195°C (from ethanol). IR spectrum, ν , cm^{-1} : 3252 (≡C–H); 2114 (C≡C); 1557, 1426, 1386 (pyrazole ring). ^1H NMR spectrum (acetone-*d*₆), δ , ppm: 3.54 s (2H, C≡CH), 6.43 s (2H, CH₂), 7.63 s (2H, 3-H), 8.17 s (2H, 5-H). ^{13}C NMR spectrum (acetone-*d*₆), δ_{C} , ppm: 66.1 (CH₂), 75.3 (CC≡CH), 80.5 (C≡CH), 104.2 (C⁴), 135.0 (C⁵), 144.0 (C³). Found, %: C 67.03; H 3.97; N 28.31. C₁₁H₈N₄. Calculated, %: C 67.34; H 4.11; N 28.55.

1,1'-Methylenebis(4-ethynyl-3,5-dimethyl-1H-pyrazole) (IVb) was synthesized in a similar way from 7 g (19 mmol) of acetylenic alcohol **IIIb** using 1.75 g (25 wt %) of KOH. Yield 3.94 g (94%), colorless crystals, mp 186–187°C (from ethanol). IR spectrum, ν , cm^{-1} : 3170 (≡C–H); 2080 (C≡C); 1550, 1480, 1390 (pyrazole ring). ^1H NMR spectrum (acetone-*d*₆), δ , ppm: 2.15 s (6H, 3-CH₃), 2.53 s (6H, 5-CH₃), 3.69 s (2H, C≡CH), 6.16 s (2H, CH₂). ^{13}C NMR spectrum (acetone-*d*₆), δ_{C} , ppm: 10.6 (5-CH₃), 12.3 (3-CH₃), 60.9 (CH₂), 76.2 (CC≡CH), 83.0 (C≡CH), 102.7 (C⁴), 145.0 (C⁵), 151.3 (C³). Found, %: C 71.78; H 6.41; N 21.94. C₁₅H₁₆N₄. Calculated, %: C 71.40; H 6.39; N 22.21.

Condensation of compound IIa with *p*-diethynylbenzene. A flask was charged with 0.6 g (1.5 mmol) of compound **IIa**, 0.189 g (1.5 mmol) of *p*-diethynylbenzene, 9 mg (3 mol %) of CuI, 12 mg (3 mol %) of triphenylphosphine, 2 ml of triethylamine, and 18 ml of pyridine. The mixture was heated to the boiling point in a stream of an inert gas, 16 mg (1.5 mol %) of [Pd(PPh₃)₂Cl₂] was added, and the mixture was stirred on heating under reflux in an inert atmosphere. After 13 h, the precipitate of oligomer **Va** (fraction 1) was

filtered off and dried. Yield 0.423 g, yellow powder-like material. The filtrate was poured into 200 ml water, and the precipitate (fraction 2) was filtered off. Yield 0.118 g. IR spectrum, ν , cm^{-1} : 2220 (C≡C); 1560, 1490, 1390 (pyrazole ring). ^1H NMR spectrum (DMSO-*d*₆), δ , ppm: 2.73–2.88 (C≡CH), 6.31–6.43 (CH₂), 7.49–8.35 (H_{arom}). Found, %: C 64.69; H 3.26; I 13.1; N 17.90. H(C₁₇H₁₀N₄)_{*n*}I. Calculated for $\bar{n} = 3$ ($\bar{M}_n = 940$), %: C 65.25; H 3.33; I 13.52; N 17.90.

The condensation of compound IIb with *p*-diethynylbenzene was performed in a similar way using 0.5 g (1.1 mmol) of compound **IIb**, 0.138 g (1.1 mmol) of *p*-diethynylbenzene, 5 mg (3 mol %) of CuI, 5 mg (3 mol %) of triphenylphosphine, 10 mg (1.5 mol %) of [Pd(PPh₃)₂Cl₂], 2 ml of triethylamine, and 15 ml of pyridine. Yield of oligomer **Vb** 0.460 g, orange powder-like material. IR spectrum, ν , cm^{-1} : 2200 (C≡C); 1560, 1480, 1350 (pyrazole ring). ^1H NMR spectrum (CDCl₃), δ , ppm: 2.09–2.26 (3-CH₃), 2.39 (C≡CH), 2.43–2.58 (5-CH₃), 6.05–6.11 (CH₂), 7.38–7.65 (H_{arom}). Found, %: C 64.0; H 4.8; I 16.5. H(C₂₁H₁₈N₄)_{*n*}I. Calculated for $\bar{n} = 2$ ($\bar{M}_n = 780$), %: C 64.61; H 4.78; I 16.26.

Oxidative polycondensation of compound IVa. Copper(I) chloride, 0.259 g (1.62 mmol), was added to a mixture of 0.151 g (0.77 mmol) of compound **IVa** and 10 ml of pyridine, and air was bubbled through the mixture over a period of 4 h at 20°C. The mixture was then poured into 200 ml of water, and the precipitate was filtered off, washed in succession with water, 10% aqueous ammonia, and water again, and dried at 60°C under reduced pressure. We thus isolated 0.100 g (68%) of oligomer **VIa** as a light yellow powder-like material. The product was purified by reprecipitation from dioxane into water. IR spectrum, ν , cm^{-1} : 2200, 2140 (C≡C); 1540, 1420, 1380 (pyrazole ring). ^1H NMR spectrum (CDCl₃), δ , ppm: 2.13 (C≡CH), 6.15 (CH₂), 7.56–7.61 (3-H), 7.69–7.76 (5-H). $\bar{M}_n = 1550$. Found, %: N 28.26. C₁₁H₆N₄. Calculated, %: N 28.85. A sample of oligomer **VIa** was obtained in a similar way at 60°C.

The oxidative polycondensation of compound IVb under different conditions (reaction time, temperature, and amount of the catalyst were varied) was performed as described above for compound **IVa**. From 0.30 g (1.19 mmol) of **IVb** and 0.25 g (2.50 mmol) of copper(I) chloride in 20 ml of pyridine (20°C, 4 h) we obtained 0.255 g (86%) of oligomer **VIb** as a light yellow powder-like material. IR spectrum, ν , cm^{-1} : 2200, 2160 (C≡C); 1550, 1480, 1360

(pyrazole ring). ^1H NMR spectrum (CDCl_3), δ , ppm: 2.12–2.18 (3- CH_3), 2.38 ($\text{C}\equiv\text{CH}$), 2.40–2.45 (5- CH_3), 5.95–6.07 (CH_2). $M_n = 4500$. Found, %: C 71.52; H 5.92; N 22.12. $\text{C}_{15}\text{H}_{14}\text{N}_4$. Calculated, %: C 71.98; H 5.64; N 22.38.

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