Iodochlorination of stilbene (1). *A.* Stilbene (257 mg, 1.42 mmol) and $KICl_2$ (370 mg, 1.56 mmol) were treated in a ball vibrational mill for 1 h, and the mixture was extracted with benzene (3×5 mL), washed successively with an aqueous sodium thiosulfate solution and water, and dried with sodium sulfate. After the solvent was removed, 2-chloro-1-iodo-1,2-diphenylethane (413 mg) was obtained, yield 85%, m.p. 131 °C (decomp.) (*cf.* Ref. 3: m.p. 131 °C).

B. Stilbene (180 mg, 1 mmol) ground in a mortar and $KICl_2$ (260 mg, 1.1 mmol) in 5 mL of CCl_4 were stirred with a magnetic stirrer for 7.5 h and allowed to stand overnight. After treatment similar to that of procedure *A* the initial compound **1** was isolated (180 mg, 100%), m.p. 123—124 °C (from benzene) (*cf.* Ref. 4: m.p. 124 °C).

Iodochlorination of methyl cinnamate (2). *A.* Methyl cinnamate (162 mg, 1 mmol) and $KICl_2$ (260 mg, 1.1 mmol) were treated in a ball vibrational mill for 4 h and allowed to stand overnight. After the usual treatment the initial ester **2** was isolated (123 mg, 76%), m.p. 32—33 °C (*cf.* Ref. 5: m.p. 33—34 °C).

B. A solution of methyl cinnamate (162 mg, 1 mmol) and $KICl_2$ (260 mg, 1.1 mmol) in 5 mL of CCl_4 was stirred with a magnetic stirrer for 4 h and treated analogously to the above procedure. A mixture was obtained (276 g) that contained, according to the data of ^1H NMR spectroscopy, 263 mg of methyl 2-chloro-1-iodo-2-phenylpropionate (yield 81%) and 13 mg (8%) of the initial ester **2**. Pure iodochloroester (120 mg, 34%) was obtained by triple recrystallization of the mixture from petroleum ether, m.p. 98—99 °C (from petroleum ether) (*cf.* Ref. 6: m.p. 97—98 °C). ^1H NMR, δ: 3.7 (s, 3 H, Me); 4.7 (d, 1 H, CHI, ^3J = 11.7 Hz); 5.1 (d, 1 H, CHCl); 7.1 (m, 5 H, Ph).

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Synthesis of new bis[*p*-(phenylethynyl)phenyl]hetarylenes and bis[*p*-(phenylglyoxalyl)phenyl]hetarylenes

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A series of new bis[*p*-(phenylethynyl)phenyl]hetarylenes was obtained by cross-coupling between heteroaromatic dibromides and phenylacetylene catalyzed by phosphine complexes of palladium in the presence of CuI and an organic base. Bis[*p*-(phenylethynyl)phenyl]hetarylenes were oxidized to the corresponding bis[*p*-(phenylglyoxalyl)phenyl]hetarylenes using the I_2—DMSO system.

Key words: phenylacetylene, cross-coupling reaction; bis[*p*-(phenylethynyl)phenyl]hetarylenes, bis[*p*-(phenylglyoxalyl)phenyl]hetarylenes; palladium, catalysis.

Bis[*p*-(phenylethynyl)phenyl]arylenes and bis[*p*-(phenylglyoxalyl)phenyl]arylenes have attracted attention of researchers as monomers for the preparation of phenyl-substituted polyphenylenes[1] and polyphenylquinoxalines.[2] Numerous representatives of both the former and the latter classes of monomers are known; however, their analogs containing divalent residues of aromatic heterocycles instead of arylene fragments have been poorly studied.

In the present work, we synthesized bis[*p*-(phenylethynyl)phenyl]hetarylenes and bis[*p*-(phenylglyoxalyl)phenyl]hetarylenes with quinoxal-2,3-diyl and

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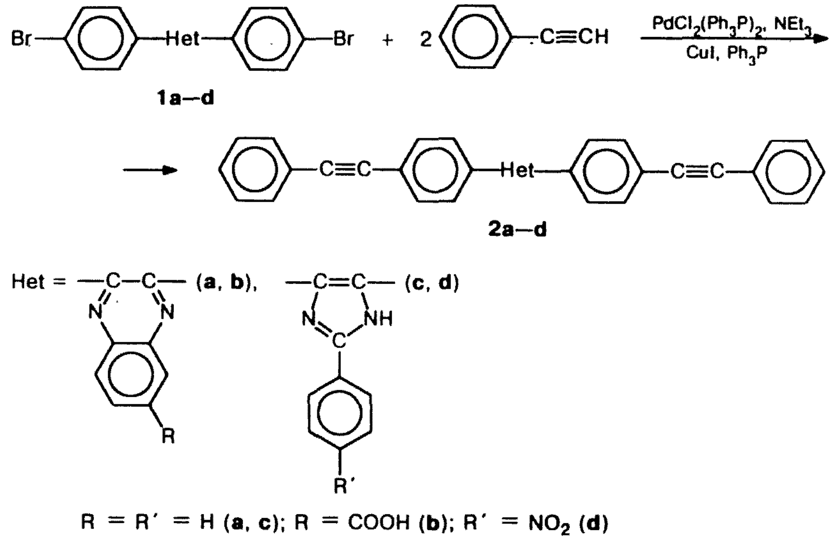
Scheme 1



2-arylimidazol-4,5-diyl fragments based on the corresponding dibromoaromatic compounds described previously.[3]

Bis[*p*-(phenylethynyl)phenyl]hetarylenes were synthesized by Pd-catalyzed cross-coupling (*cf.* Ref. 4) of the initial dibromides **1a—d** with double the molar amounts of phenylacetylene as shown in Scheme 1.

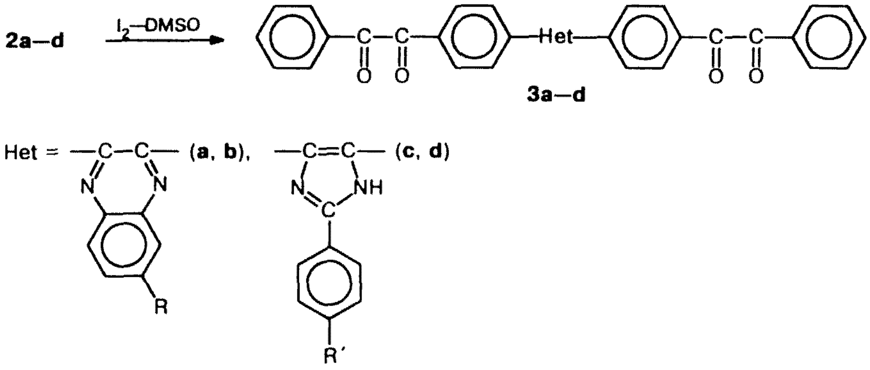
Some physicochemical and spectral parameters of the resulting bis[*p*-(phenylethynyl)phenyl]hetarylenes **2** are listed in Table 1. The structures of compounds **2a—d** were confirmed by the data of elemental analysis and by their Raman spectra, which contain absorption bands at 2212—2221 cm^{-1} typical of the stretching vibrations of C≡C groups.[5] The data of Table 1 indicate that the yields of compounds **2a—d** are relatively low; in particular, monosubstituted ethynyl derivatives are formed along with the target bis[*p*-(phenylethynyl)phenyl]hetarylenes **2a—d.**[6]

Bis[*p*-(phenylethynyl)phenyl]hetarylenes **2a—d** were oxidized to the corresponding bis[*p*-(phenylglyoxalyl)phenyl]hetarylenes **3a—d** using the I_2—DMSO system[7] (Scheme 2).

Table 1. Characteristics of bis[*p*-(phenylethynyl)phenyl]hetarylenes **2a—d** and bis[*p*-(phenylglyoxalyl)phenyl]hetarylenes **3a—d**

Compound	Yield (%)	M.p. /°C	Found/Calculated (%)			Molecular formula	Raman spectrum, ν(C≡C)/cm^{-1}
			C	H	N		
2a	20	209—210	89.68 89.59	4.66 4.59	5.77 5.77	$C_{36}H_{22}N_2$	2212
2b	19	306—307	84.47 84.38	4.30 4.21	5.16 5.32	$C_{37}H_{22}N_2O_2$	2215
2c	21	254—256	89.63 89.49	5.63 5.64	4.81 4.27	$C_{37}H_{24}N_2$	2219
2d	34	267—268	82.05 82.05	4.13 4.28	7.49 7.76	$C_{37}H_{23}N_3O_2$	2218
3a	78	205—207	79.15 79.10	4.17 4.05	5.21 5.13	$C_{36}H_{22}N_2O_4$	
3b	89	192—193	75.00 75.24	3.70 3.75	4.51 4.74	$C_{37}H_{22}N_2O_6$	
3c	86	147—148	79.13 79.26	4.26 4.31	4.83 4.99	$C_{37}H_{24}N_2O_4$	
3d	79	161—163	73.41 73.38	3.93 3.82	6.80 6.93	$C_{37}H_{23}N_3O_6$	

Scheme 2



R = R′ = H (**a**, **c**); R = COOH (**b**); R′ = NO_2 (**d**)

The structures of the resulting compounds **3a—d** were confirmed by the data of elemental analysis and by their IR spectra, which contain absorption bands at 1680 cm^{-1} typical of stretching vibrations of C=O groups.[8] Some physicochemical and spectral parameters of the resulting bis[*p*-(phenylglyoxalyl)phenyl]hetarylenes **3** are listed in Table 1.

The fact that the central heterocyclic fragments in the monomers synthesized are asymmetrical provides reason to expect that the polymers based on these monomers should exhibit enhanced solubility in organic solvents, while the monomers containing carboxyl groups (**2c** and **3c**) should yield water-soluble polymers. The presence of polar nitro groups in monomers **2d** and **3d** makes it possible to prepare polymers with nonlinear optical properties from them.

Experimental

Raman spectra were recorded on a U 1000 spectrometer with excitation by the 5145 Å line from an ILA-2 100-MW Ar^+-laser. IR spectra were obtained on a UR-20 instrument for samples in Vaseline oil. The solvents and phenylacetylene were purified by standard procedures. Compounds **1a—d** were prepared by a previously described procedure.[3]

2,3-Bis[*p*-(phenylethynyl)phenyl]quinoxaline (2a). Ph_3P (0.066 g, 0.25 mmol) and CuI (0.067 g, 0.35 mmol) were added in an argon flow to a solution of 2,3-di(4-bromophenyl)quinoxaline (**1a**) (4.40 g, 10 mmol) and phenylacetylene (2.04 g, 20 mmol) in 160 mL of a mixture of dimethylacetamide (DMAA) and triethylamine (1 : 1). The reaction mixture was stirred for 15 min, and $PdCl_2(Ph_3P)_2$ (0.07 g, 0.1 mmol) was added. The mixture was heated to 80 °C and kept at this temperature for 10 h, while the course of the reaction was monitored by TLC. Then the reaction mixture was cooled to room temperature, and the precipitate that formed was filtered off and washed with 10% HCl (2×50 mL), with water to a neutral reaction of the medium, and with ethanol. It was then dried *in vacuo* to give compound **2a**, yield 20%, m.p. 209—210 °C (from BuOH).

Compounds **2b—d** were synthesized in a similar way (see Table 1).

2,3-Bis[*p*-(phenylglyoxalyl)phenyl]quinoxaline (3a). Iodine (2.54 g, 10 mmol) was added to a solution of bis[*p*-(phenylethynyl)phenyl]hetarylene **2a** (2.41 g, 5 mmol) in 50 mL of DMSO. The reaction mixture was heated with stirring to 155 °C, kept at this temperature for 22 h, cooled to ~20 °C, and poured into a tenfold excess of water. The precipitate was filtered off, washed with a 1% solution of $Na_2S_2O_3$ to remove excess iodine, with water to a neutral reaction of the medium, and with ethanol. It was then dried *in vacuo* to give compound **3a**, yield 78%, m.p. 205—207 °C (from BuOH).

Compounds **3b—d** were synthesized in a similar way (see Table 1).

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