DOI: 10.1002/ejoc.200600357

2-Arylazo-1-vinylpyrroles: A Novel Promising Family of Reactive Dyes

Boris A. Trofimov,*[a] Elena Yu. Schmidt,[a] Al'bina I. Mikhaleva,[a] Alexander M. Vasil'tsov,[a] Alexey B. Zaitsev,[b] Natalia S. Smolyanina,[a] Elena Yu. Senotrusova,[a] Andrey V. Afonin,[a] Igor' A. Ushakov,[a] Konstantin B. Petrushenko,[a] Olga N. Kazheva,[c] Oleg A. Dyachenko,[c] Vladimir V. Smirnov,[d] Alexander F. Schmidt,[d] Marina V. Markova,[a] and Ludmila V. Morozova[a]

Keywords: 2-Arylazo-1-vinylpyrroles / Azo coupling / Conformation / Copolymerization / 1-Vinylpyrroles / Dyes

New reactive dyes, 2-arylazo-1-vinylpyrroles, have been synthesized in 52–94 % yield by a modified azo coupling of readily accessible 1-vinylpyrroles with arenediazonium hydrocarbonates in aqueous ethanol (≈3:1) at 0 °C. The λ_{max} values for the UV/Vis absorption of the dyes ranges from 377.8–480.6 nm with $\log\varepsilon$ = 4.11–4.99, and this strongly depends on the substituent structure both in the pyrrole and the benzene ring, and is indicative of highly polarizable and tunable chromophores. X-ray, ^{1}H NMR spectroscopic and quantum chemical studies [B3LYP/6-311 (d,p)] show the *E*,*anti*,*anti* isomer of the dyes to be the most stable under normal conditions. The dyes are reversibly protonated and complex to BF_3 with a color change. Their copolymerization across the vinyl group affords intrinsically colored copolymers. They have also been shown to act as good ligands in the Pd-catalyzed Heck alkene arylation. Thus, the properties of the novel dyes are promising for creating new molecular switches, memory and recording devices, acid-base and metal sensors, as well as transition-metal complex catalysts.

Introduction

Aryl- and hetarylazopyrrole dyes have been attracting much attention over the past decade because of their rapidly increasing role in the design of advanced materials and devices.[1–12] The insertion of an azo group between dipyrrole moieties by anodic coupling of 2,2′-azopyrrole results in polyazopyrrole, the first reported narrow-bandgap polyconjugated pyrrole-based polymer, which exhibits a dramatic drop in the energy gap (from 2.5–2.8 eV to about 1 eV when compared to polypyrrole).[1,2,4,9] This material has one of the narrowest bandgaps among the neutral pyrrole-based conducting polymers.[9] The *E*/*Z*-isomerizable N=N double bond within a conducting chain can work as a molecular switcher, making the aryl- or hetarylazopyrrolic systems promising candidates for molecular devices.[9] 4-(1-*n*-Octadecylpyrrol-2-ylazo) benzoic acid, a representative of arylazopyrroles, affords Langmuir-Blodgett films with electrically conducting and non-linear optical (NLO) properties.[3]

Diverse aryl- and hetarylazopyrroles,[5,6] and related metal chelates[7,8] have extensively been patented as thermal transfer printing dyes[5,6] and optical recording materials.[7,8] The latter can be recorded and read by light with a wavelength of 600–720 nm at good light speeds and is also stable enough for storage on DVD R systems using semiconductor laser beams with a shorter wavelength.

Chromonophores (reagents changing color in the presence of ions) with 2,5- or 2,3-bis(azo) pyrrole entities in crown ether macrocycles make the membrane electrodes potassium-selective.[10]

The pyrrolylazo entity, when combined with a suitable heteroarene acceptor, exhibits a donor capacity in the design of chromophoric self-assembled thin films with NLO properties, which have the potential to be applied as photonic and electrooptic materials.[11] For this purpose, highly polarizable push–pull systems with large intramolecular

[a] A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 Favorsky St., Irkutsk 664033, Russian Federation
Fax: +7-3952-419346
E-mail: boris_trofimov@irioch.irk.ru
[b] Department of Organic Chemistry, the Arrhenius Laboratory, Stockholm University,
10691 Stockholm, Sweden
Fax: +46-8-154908
E-mail: zaitsev@organ.su.se
[c] Institute of Problems of Chemical Physics of the Russian Academy of Sciences,
1 Semenov's Av., Chernogolovka, Moscow District 142432, Russian Federation
Fax: +7-096-5155420
E-mail: koh@icp.ac.ru
[d] Irkutsk State University,126 Lermontov St., Irkutsk, 664033, Russian Federation,
Fax: +7-3952-426856
E-mail: aschmidt@chem.isu.ru

charge-transfer excitation, such as 5-(1-methylpyrrol-2-ylazo)quinoline and particularly, its *N*-methyl triflate, have been employed.[11] Imperative for active second-order NLO chromophores is a noncentrosymmetric charge distribution as it is in the above hetarylazopyrroles.

A recent DFT study[12] has revealed significantly lower excitation energies for N=N spaced pyrroles with aromatic or heteroaromatic rings relative to those of similar but directly linked π-systems. This offers an additional opportunity in the search for materials with improved electronic and optical properties.

In spite of all these spectacular recent strides in the chemistry and applications of azopyrrolic dyes, little is known about their vinyl congeners. Meanwhile, the vinyl substituent could multiply the potential of these compounds, which imparts upon them diverse multi-faceted extra reactivity including polymerizability. A limited, though important family[13–16] of such compounds are the long-known azo coupled bile pigments (bilirubin and related species). The bilirubin serum and its conjugates are commonly measured in clinics by an azo coupling method.[16] The synthesis of bilirubin-based C-vinyl arylazopyrroles helped to elucidate the mechanism of *anti*-oxidation by bilirubin and its metabolites as well as their important role as *anti*-oxidants to control various oxidative stresses in humans.[16] Apart from this quite specific class of arylazo vinylpyrroles, to the best of our knowledge, no similar dyes with vinyl substituents in the pyrrole ring, especially at the nitrogen atom, are reported to date.

To meet a challenge and introduce such a promising family of dyes to chemistry, material science, and medicine, we have explored two possible general approaches to the synthesis of 2-arylazo-1-vinylpyrroles **3**–**22**: (*a*) direct vinylation of (arylazo)pyrroles **1** by acetylene and (*b*) azo coupling of 1-vinylpyrroles **2** with arenediazonium salts. Contrary to expectation, the former approach, on first glance, appeared to be the most obvious and straightforward, but in actuality turned out to be a failure, while the latter proved to be both facile and universal (Scheme 1).

In this paper we discuss the main features of the synthesis of 2-arylazo-1-vinylpyrroles **3**–**22**, peculiarities of their structure, and some fundamental properties.

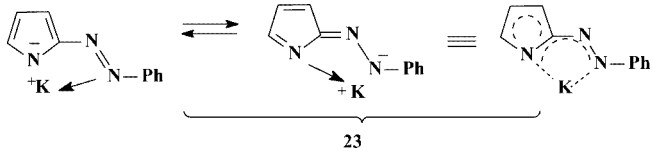
Results and Discussion

Synthesis

As mentioned above, first, we have studied the direct vinylation of 2-arylazopyrroles **1** with acetylene using 2-phenylazopyrrole ($R^1 = R^2 = R^3 = H$) as an example (Scheme 1, *a*). To this end, the superbasic catalytic system KOH/DMSO has been employed under conditions (110 °C, at room temperature initial acetylene pressure = 14 atm, 2 h) that have proved optimal for vinylation of diverse pyrroles.[17] However, the expected 2-phenylazo-1-vinylpyrrole (**3**) is not discernible in the reaction mixture. In the analysis of the ^{1}H NMR spectrum of the crude product, signals for the *N*-vinyl group are not observed. Instead, along with signals of starting 2-phenylazopyrrole **1** [δ = 9.23 (br. s, 1 H, NH), 7.76 (d, 2 H, H_o), 7.43 (m, 2 H, H_m), 7.36 (t, 1 H, H_p), 6.99 (m, 1 H, 5-H), 6.90 (m, 1 H, 3-H), 6.99 (m, 1 H, 4-H) ppm], two unassignable multiplets (δ = 3.4 and 3.8 ppm) and a quartet (δ = 4.7 ppm) with intensities close to those of the starting pyrrole **1** are present.

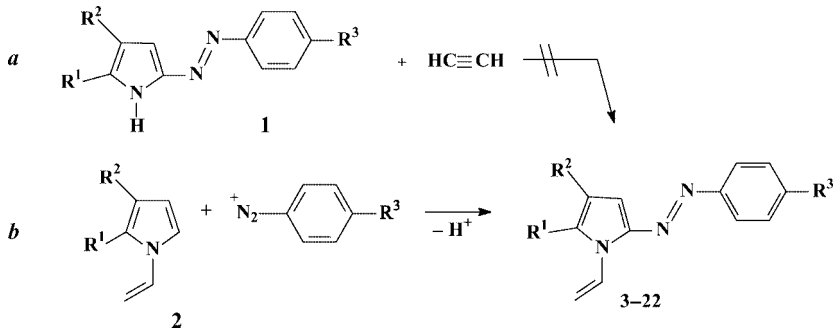
The ^{1}H NMR spectrum of a crude product obtained at a higher temperature (130 °C) contains no signals representing the starting 2-phenylazopyrrole (in the region of 1.0–7.5 ppm, broad multiplets and singlets at δ = 1.5, 2.5, 3.4, 5.0, 5.8, 5.6 ppm were observed), indicating its complete decomposition.

The results may be rationalized in terms of a strong chelation between the potassium cation and the azopyrrole salt **23** (Scheme 2) similar to that claimed in the patents.[7,8]



Scheme 2. Tentative chelating of potassium cation by 2-phenylazopyrrole.

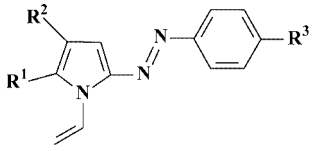
Obviously, such an interaction should greatly decrease the nucleophilicity of the pyrrole anion and hence suppress its vinylation.



Scheme 1. Synthesis of 2-aryazo-1-vinylpyrroles (for R^1, R^2 and R^3 see Table 1).

Although the azo coupling of NH-pyrroles with arenediazonium cations can be successful within a broad pH range,[11,13,14,16] in the case of 1-vinylpyrroles **2** the reaction must be carried out in neutral or basic media (pH ≥ 7) and at a temperature around 0 °C, otherwise in the presence of acids, hydrolysis or dimerization and oligomerization involving the *N*-vinyl group occur.[17a,17b] Therefore, to keep the *N*-vinyl group intact, the azo coupling of 1-vinylpyrroles **2** with arenediazonium cations (Scheme 1 *b*, Table 1) was conducted in an aqueous ethanolic (≈3:1) solution of $NaHCO_3$ (pH ≈ 7) at 0 °C for 2 h. Under these uniform (not optimized for each couple) conditions, the yields of the coupling products **3**–**22** ranged within 52–94%.

Table 1. Yields of 2-arylazo-1-vinylpyrroles **3**–**22** and their UV/Vis spectral characteristics in MeCN.

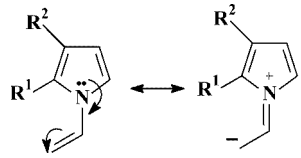


Azopyrrole	R^1	R^2	R^3	Yield [%]	λ_{max} [nm]	log ε
3	H	H	H	80	383.1	4.32
4	H	H	EtO	52	377.8	4.91
					393.0 (sh)	4.85
					428.5 (sh)	4.71
5	H	H	NO_2	84	413.4	4.85
6	Me	H	H	80	397.5	4.62
7	Me	H	EtO	76	402.0	4.93
8	Me	H	NO_2	85	439.8	4.54
9	Me	H	Br	76	405.8	4.69
10	Me	H	PhN_2	79	445.1	4.72
11	$(CH_2)_4$		H	87	408.8	4.84
12	$(CH_2)_4$		EtO	80	410.3	4.41
					451.1 (sh)	4.43
13	$(CH_2)_4$		NO_2	94	470.8	4.77
14	$(CH_2)_4$		Br	82	416.4	4.82
					449.6 (sh)	4.74
15	$(CH_2)_4$		PhN_2	81	476.8	4.68
16	Ph	H	H	53	407.3	4.81
17	Ph	H	NO_2	56	454.2	4.89
18	4-$MeOC_6H_4$	H	H	57	414.9	4.64
19	4-$MeOC_6H_4$	H	NO_2	56	477.6	4.99
20	2-furyl	H	H	53	–	–
21	2-thienyl	H	H	53	418.6	4.48
22	2-thienyl	H	NO_2	79	480.6	4.11

The azo coupling thus realized represents a typical aromatic electrophilic substitution, hence electron-releasing substituents on the pyrrole ring (R^1, R^2) and electron-withdrawing ones in the arenediazonium cation should facilitate the reaction, which is in agreement with the yield trend seen from Table 1. Indeed, when a π-donor (EtO) is introduced on the benzenediazonium cation, the yield considerably drops (from 80 to 52%, cf. pyrroles **3** and **4**, Table 1), whereas for 4-nitrobenzene diazonium cation with unsubstituted (R^1 = R^2 = H) and donor-substituted [R^1 = Me, R^2 = H; R^1–R^2 = $(CH_2)_4$] 1-vinyl pyrroles, it is always high (84–94%, Table 1). Also high (76–81%) are the yields for the cases of other acceptor substituents in the arenediazonium cations (R^3 = Br, PhN_2). At the same time, introduction of acceptor substituents (Ph, 4-$MeOC_6H_4$, 2-furyl, 2-thienyl) into the pyrrole moiety leads to an adverse yield trend (53–57%).

As exemplified by the coupling of 1-vinyl-4,5,6,7-tetrahydroindole **2** [R^1–R^2 = $(CH_2)_4$] with the benzenediazonium cation, with short reaction times (1 h) the conversion of pyrrole **2** decreases (75%) and the yield of the corresponding coupling product **11** drops from 87 to 72%. At a higher temperature (50–60 °C) the yield of the coupling product **11** becomes negligible (≈2%) because of the rapid decomposition of the arenediazonium salt.

Because of the electron-withdrawing effect of the vinyl group and the noticeable competition for the *p*-π-conjugation with the nitrogen atom,[18a] which persists even in 1-vinylpyrrolium cations,[18] the reaction is strictly regiospecific. In neither case are the coupling products at the pyrrole *β*-position identified in the reaction mixture.



Also, despite the high nucleophilicity of the *N*-vinyl group, under the selected conditions it remains essentially unreactive towards the arenediazonium cations.

An advantage of the developed synthetic approach, apart from its generality and efficiency, is that it is based on available starting materials, 1-vinylpyrroles, which are commonly prepared in a one-pot procedure by the Trofimov reaction from ketoximes and acetylene[17a,17b,19] or by its newer version[20] directly from ketones and acetylene.

UV/Vis and ^{13}C NMR Spectra

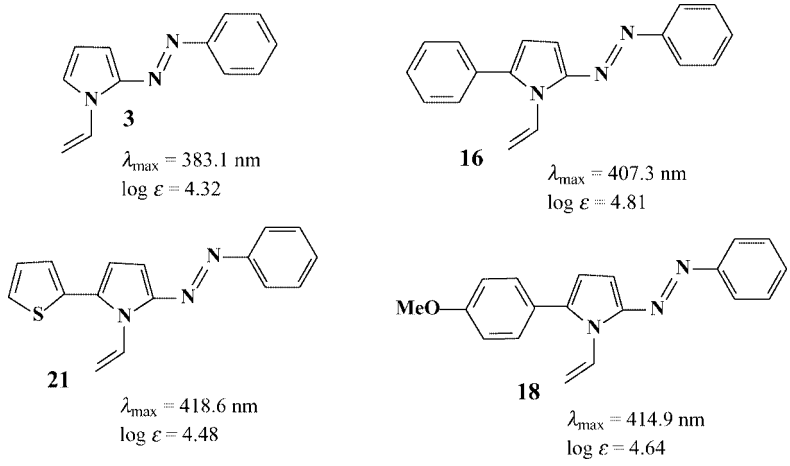
Table 1 presents UV/Vis optical spectroscopic data (λ_{max}, log ε) for 2-arylazo-1-vinylpyrroles **3**–**22** in acetonitrile. Analysis of the structure effects on the λ_{max} and log ε values reveals a noticeable push–pull character of the synthesized dyes. Indeed, both donor substituents in the pyrrole ring [Me, $(CH_2)_4$] and acceptor substituents in the areneazo counterpart (NO_2, PhN_2) promote a sizeable (up to about 100 nm) bathochromic shift (Δλ) relative to that of parent compound **3** ($\Delta\lambda = \lambda^{i}_{max} - \lambda^{3}_{max}$), which in most cases is accompanied by an increase in the absorption intensity, the Δlog ε value reaches 0.67 ($\Delta\log\varepsilon = \log\varepsilon^{i} - \log\varepsilon^{3}$). Substituents such as MeO, EtO and Br, which are simultaneous π-donors and σ-acceptors by nature, display the complex response that is manifested both in appearance of the shorter wavelength absorption maxima and the longer wavelength

shoulders (for **3** → **4**: λ_{max} = 383.1→ 377.8, 393.0 sh, 428.5 nm sh; for **11** → **12**: λ_{max} = 408.8 → 410.3, 451.1 nm sh). The multiplet nature of the absorption is likely a result of the different orientation (conformation) of the EtO group with respect to the benzene ring (*syn* or *anti*; planar or non-planar). The bathochromic shift and absorption intensity are also expectedly increased with the extension of the chromophore π-core. For phenyl and 2-thienyl substituents on the pyrrole ring this effect successfully competes with their σ-acceptor adverse contributions (cf. spectra of **3**, **16**, **18**, and **21**, Scheme 3).

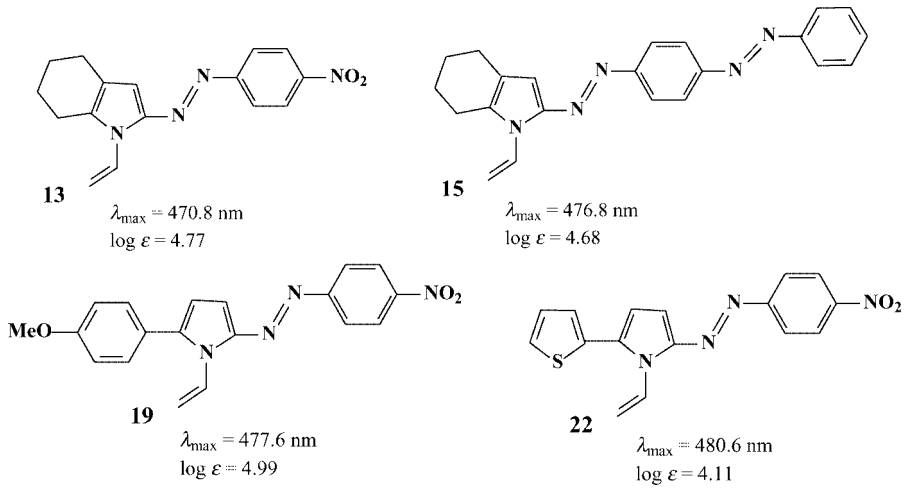
Especially strong bathochromic shifts and an increase in the absorption intensity are observed when all these effects are in one direction (a donor in the pyrrole ring, an acceptor in the areneazo moiety, and general extension of π-conjugation) like those in dyes **13**, **15**, **19**, **22** (Scheme 4).

The remarkable optical response to the structure effects in the synthesized dyes is indicative of their highly polarizable π-electron core and suggests that these new chromophores possess hyperpolarizability comparable to, or higher than, that of the azinium-(N=N bridge)-pyrrole systems, which have recently been successfully employed as building blocks for NLO materials.[11] Indeed, such dyes with noncentrosymmetric charge distribution are of key value in for the design of efficient second-order NLO-phores.[11]

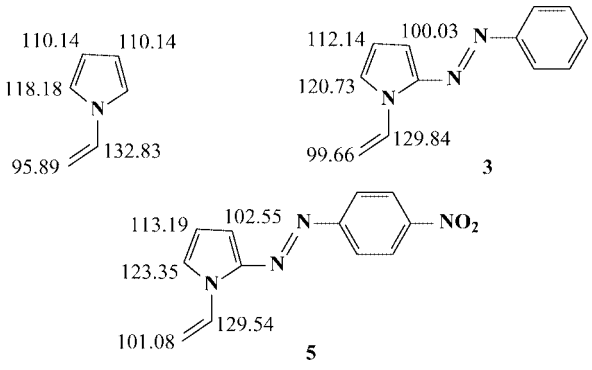
The ^{13}C NMR spectra confirm a significant charge transfer from the vinylpyrrole moiety to the arylazo group and a high polarizability of the whole dye molecules. This is manifested by a strong downfield shift of the C-4 and C-5 signals (2–3 ppm and 2–7 ppm, respectively) and an upfield shift of the C-3 signals (7–10 ppm) compared to the corresponding values of the same pyrroles without arylazo substituents[21] (Scheme 5). Correspondingly, the vinyl group is considerably depolarized: for the 5-unsubstituted dyes, the C_α signals are shifted upfield (1–3 ppm), while the C_β signals display a downfield shift (4–11 ppm) relative to the corresponding values of the unsubstituted *N*-vinylpyrrole[21] (Scheme 5). The substituents at the C-5 atom, which force the vinyl group to deviate out of the pyrrole plane even more, decrease the *p*-π-conjugation of the double bond with the nitrogen atom (cf. 1-vinylpyrrole, 2-methyl-1-vinylpyrrole,[22] the pyrroles **3** and **6**, Scheme 5).



Scheme 3. Effects of the extended π-systems on the UV/Vis spectral characteristics of 2-arylazo-1-vinylpyrroles.



Scheme 4. Combined structure effects on the UV/Vis spectral characteristics of 2-arylazo-1-vinylpyrroles.



Scheme 5. The charge redistribution in the *N*-vinylpyrrole moiety under the influence of arenylazo substituents as evidenced from ^{13}C chemical shifts (ppm).

Since the ^{13}C chemical shifts of the corresponding carbon atoms and atomic charges are roughly inversely related, all the changes observed in the ^{13}C NMR spectra of 2-arylazo-1-vinylpyrroles relative to those of 1-vinylpyrroles do reflect a remarkable electron density displacement towards the azo group.

The distant NO_2 substituent in the benzene ring renders a noticeable charge displacement not only from the most remote C-5 and C-4 atoms of the pyrrole ring, but from the vinyl group as well (cf. pyrroles **3** and **5**, Scheme 5), thus again demonstrating the easy electron communication within the whole dye molecules.

X-ray Structure

Dyes **3**–**22** are deeply colored (green, orange, red, crimson) crystals or powders melting in the range of 52–180 °C (mostly 60–120 °C).

The main crystallographic data and the parameters of the X-ray structure refinement of 2-phenylazo-1-vinylpyrrole (**3**), a parent compound of the family, are given in Table 2. Selected bond lengths and angles are listed in Table 3. According to these parameters, the pyrrole ring of **3** is distorted, in agreement with the expected charge transfer. In Scheme 6, some of the most pronounced changes in the bond lengths and angles in comparison with those of unsubstituted pyrrole[14] (in brackets) are shown.

Indeed, the bonds N(1)–C(5), C(3)–C(4), and N(2)–C(2) are considerably shortened, while the bonds C(2)–C(3), C(4)–C(5), and N(2)–N(3) are lengthened compared to the normal bond length in pyrroles[14] and standard C–N and N=N bond lengths from the reference.[23] Correspondingly, the angles C(5)–N(1)–C(2) and C(3)–C(2)–N(1) are changed in opposite directions (Scheme 6). These structural distortions are explicable by a contribution of the quinoid resonance structure **B** to the basic structure **A** (Scheme 6) and confirm the intramolecular charge-transfer from the pyrrole moiety to the phenylazo counterpart.

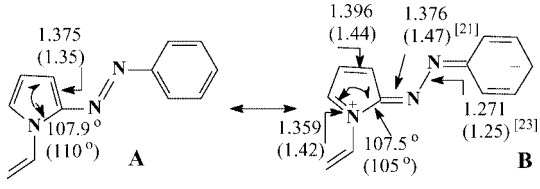
Crystals of pyrrole **3** are built from crystallographically independent molecules $C_{12}H_{11}N_3$ (Figure 1) and have a parquet structure (Figure 2). The molecules are paired by a symmetry center in a "head to tail" manner (Figure 3).

Table 2. Crystallographic data and structure refinement for 2-phenylazo-1-vinylpyrrole (**3**).

Empirical formula	$C_{12}H_{11}N_3$
Molecular mass	197.24
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	6.702(1)
b [Å]	11.869(2)
c [Å]	13.252(3)
β [°]	92.91(2)
V [Å^3]	1052.8(3)
Z	4
λ [Å]	0.7107 (Mo)
Calculated density [Mg·m^{-3}]	1.24
μ [mm^{-1}]	0.077
Reflections collected	1943
Independent reflections	1784
Reflections for [$F_o > 4\sigma(F_o)$]	1420
Number of parameters	181
$(2\theta)_{max}$ [°]	49.94
Interval for h	$0 \le h \le 7$
Interval for k	$0 \le k \le 14$
Interval for l	$-15 \le l \le 15$
R – factor [$F_o > 4\sigma(F_o)$]	0.037

Table 3. Selected X-ray bond lengths [Å] and bond angles [°] for 2-phenylazo-1-vinylpyrrole (**3**).

Bonds	
N(1)–C(5)	1.359(2)
N(1)–C(2)	1.390(2)
N(1)–C(6)	1.409(2)
N(2)–N(3)	1.271(1)
N(2)–C(2)	1.376(2)
N(3)–C(8)	1.424(2)
C(2)–C(3)	1.375(2)
C(3)–C(4)	1.396(2)
C(4)–C(5)	1.349(2)
C(6)–C(7)	1.288(2)
Angles	
C(5)–N(1)–C(2)	107.5(1)
C(5)–N(1)–C(6)	127.8(1)
C(2)–N(1)–C(6)	124.7(1)
N(3)–N(2)–C(2)	113.7(1)
N(2)–N(3)–C(8)	113.4(1)
C(3)–C(2)–N(2)	134.8(1)
C(3)–C(2)–N(1)	107.9(1)
N(2)–C(2)–N(1)	117.3(1)
C(2)–C(3)–C(4)	107.0(1)
C(5)–C(4)–C(3)	108.1(1)
C(4)–C(5)–N(1)	109.4(1)
C(7)–C(6)–N(1)	125.3(2)
C(9)–C(8)–N(3)	125.2(1)
C(13)–C(8)–N(3)	115.5(1)



Scheme 6. The structure distortion in 2-phenylazo-1-vinylpyrrole (**3**) versus standard bond lengths and angles.

Molecules in the pairs are parallel, and the distance between the planes formed by the pyrrole, the benzene rings, and the azo group is 3.62 Å. The dihedral angle between the planes of different molecular pairs is 74.4°.

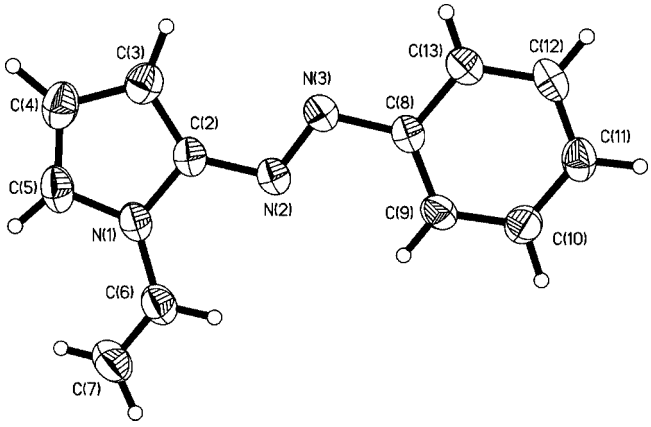


Figure 1. ORTEP diagram for 2-phenylazo-1-vinylpyrrole **3**.

The azo group of pyrrole **3** has the *E* configuration with *anti* orientation of the N(1) and N(3) atoms and lies in the plane of the pyrrole and benzene rings (the dihedral angles are 0° and 3.5°, respectively). The dihedral angle between the vinyl group plane and the pyrrole ring is also small (–7.1°) with *anti* orientation to the azo group. Thus, the whole molecule of 2-phenylazo-1-vinylpyrrole **3** is essentially planar securing the maximal possible conjugation and intramolecular charge transfer through the four interacting π-systems.

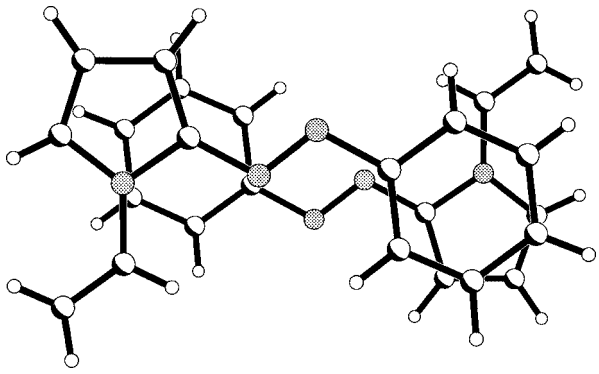


Figure 3. Molecular pairing of 2-phenylazo-1-vinylpyrrole **3**.

It is noteworthy that the distance between the N(2) atom and the α-H atom of the vinyl group (2.50 Å) is shorter than the van der Waals radii of these atoms (2.75 Å).[24] Such close contacts are often explained[24–27] by weak hydrogen bonding, here C–H···N.[28] In spite of the fact that the contact is not close enough,[29] the conclusion is supported by NMR spectroscopy (see below).

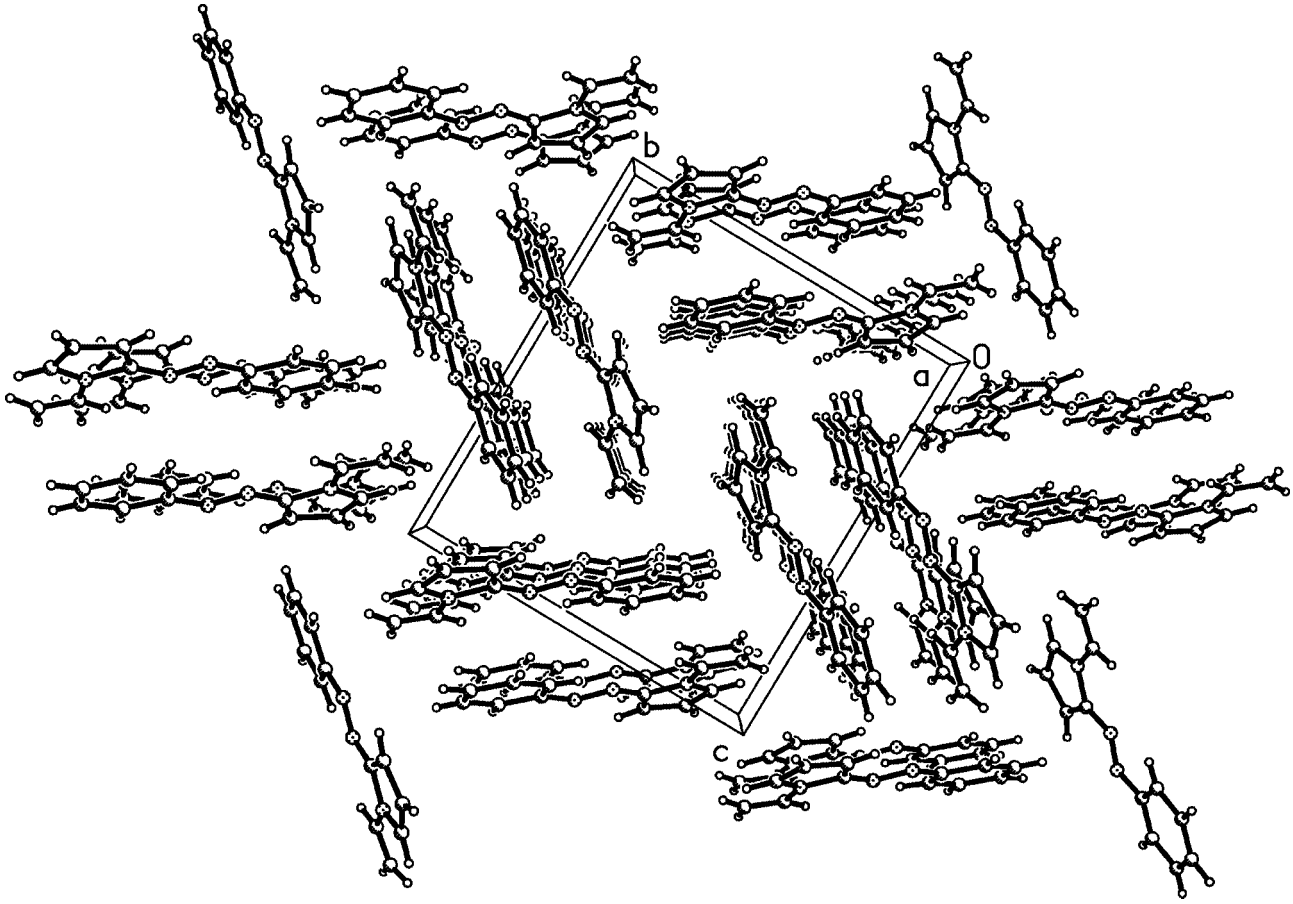
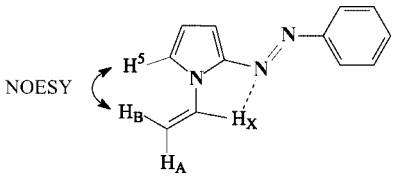


Figure 2. Parquet structure of 2-phenylazo-1-vinylpyrrole **3**.

NMR and Quantum Chemical Study of the Isomerism

Discerning the most stable configuration and conformation and their energy differences of the synthesized dyes is necessary for further investigations of the reversible configurational and/or conformational interconversions of their molecules under electromagnetic, chemical, or heat stimuli, which are the most important aspects in the design of novel molecular switches, memory, and recording devices.

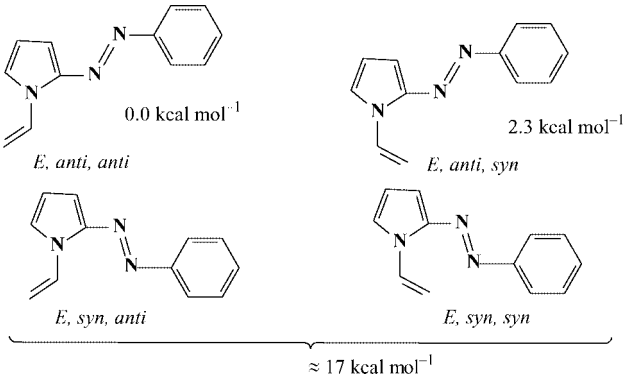
The major feature of the ^{1}H NMR spectrum of azopyrrole **3** is that the signal of its vinyl α-hydrogen H_X is unusually far downfield (δ = 7.87 ppm), while for 2-substituted 1-vinylpyrroles, the chemical shift of this hydrogen is commonly in the range of 6.6–6.9 ppm, depending weakly on the substituent effect.[28] This strong downfield shift of the H_X signal agrees with the above X-ray evidence of a weak intramolecular C–H_X···N(2) bond (Scheme 7).



Scheme 7. The C–H_X···N hydrogen bonding in 2-phenylazo-1-vinylpyrrole (**3**).

In the 2D NOESY spectrum of azopyrrole **3** the H_B–5-H cross-peak (Scheme 7) indicates that the *anti* orientation of the double bond to the azo group, observed in the crystal state, persists also in solution, evidently due to the C–H_X···N(2) bonding.

Quantum chemical calculations [B3LYP/6-311(d,p)] for azopyrrole **3** has shown that the global energy minimum does correspond to the *E* configuration of the azo group with both the *anti* orientation of the N(1) and N(3) atoms and the *anti* orientation of the double bond relative to the azo group (*E*,*anti*,*anti* isomer), Scheme 7. The isomer with *syn* configuration of the double bond to the azo group (*E*,*anti*,*syn* form) is 2.3 kcal mol^{-1} less energetically favorable. The conformations having a *syn* disposition of the N(1) and N(3) atoms (*E*,*syn*,*anti* and *E*,*syn*,*syn* isomers) with their energy 17 kcal mol^{-1} higher than that of *E*,*anti*,*anti* isomer are certainly much less preferred under normal conditions (Scheme 8).



Scheme 8. Computed [B3LYP/6-311(d,p)] energy differences for conformations of 2-phenylazo-1-vinylpyrrole **3**.

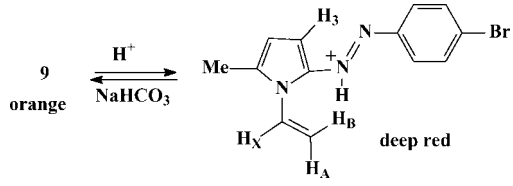
From the optimized geometry it follows that the most energetically preferred *E*,*anti*,*anti* isomer of dye **3** is completely planar with the C–H_X···N(2) distance equal to 2.40 Å (the X-ray experimental distance in the crystal form is 2.50 Å). Thus, the calculated structure corresponds well to that derived from the X-ray analysis of the crystal.

Reactivity

Protonation

Unlike alkyl- or aryl-substituted 1-vinylpyrroles,[18] the *N*-vinyl group in 2-arylazo-1-vinylpyrroles **3**–**22** remains intact in the presence of excess strong acids at ambient temperature for several hours. Meanwhile, upon addition of trifluoromethanesulfonic or trifluoroacetic acids to azopyrroles **9** or **12** in benzene or $CHCl_3$, the orange solution color turns instantly deep red thus demonstrating the capacity of the dyes to serve as pH indicators or as acidity function sensors.

The protonated center is assumed to be the N(2) atom of the azo moiety (Scheme 9), since it is the atom that participates in the intramolecular hydrogen bonding C–H_X···N(2) and its computed [B3LYP/6-311(d,p)] Mulliken atomic charge exceeds that of the N(3) atom (–0.23 and –0.22, respectively). Other evidence in favor of this assumption are the following: a downfield shift of signal for the hydrogen atom at the pyrrole position 3-H (the closest to the N(2) atom), is very large (for azopyrrole **9**, $\Delta\delta$ = +1.12 ppm) and the signal for the β-vinyl hydrogens H_A and H_B are also strongly shifted downfield (for the same pyrrole **9** $\Delta\delta$ = +0.66 and 0.28 ppm, respectively), while the α-vinyl hydrogen H_X resonates upfield ($\Delta\delta$ = –0.31 ppm). All these changes are indicative of a remarkable decrease in the *p*-π-conjugation in the *N*-vinyl group[18] because of the strong electron-withdrawing effect of the N(2)-protonated azo group and the breaking of the H_X···N(2) hydrogen bond (Scheme 9).



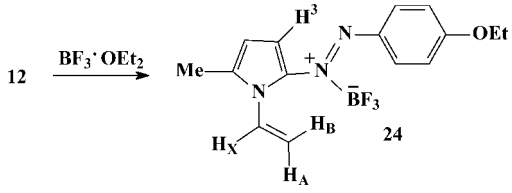
Scheme 9. Reversible protonation of 2-(4-bromophenylazo)-5-methyl-1-vinylpyrrole (**9**).

Neutralization of the acidic solution of the dyes completely restores their initial color and ^{1}H NMR spectra.

Complexation with BF_3

Upon treatment of dye **12** with BF_3·OEt_2 in benzene or $CHCl_3$, a violet solution (λ_{max} = 537.8 nm, log ε = 4.60, in benzene) of complex **24** is formed. From the ^{1}H NMR

spectrum it may be assumed that the coordination, like the protonation, occurs at the N(2) site of the azo group (Scheme 10), since it is accompanied by similar shifts of the hydrogen signals [$\Delta\delta$ = +0.91 (3-H), +0.42 (H_A), +0.20 (H_B), –0.32 (H_X) ppm].



Scheme 10. Complexation of 2-(4-ethoxyphenylazo)-1-vinyl-4,5,6,7-tetrahydroindole **12** with BF_3·OEt_2.

A few hours later, the signal of 3-H disappears and those of the vinyl group broaden, which indicates further transformations that involve the pyrrole ring without the expected polymerization across the double bond.

Unlike this result, dye **9** in the presence of BF_3·OEt_2 undergoes polymerization, probably because of the weaker donating power of the 5-methyl substituent (compared to that of the 4,5-fused cyclohexane moiety) that decreases the pyrrole ring reactivity with respect to the vinyl group, hence vinyl polymerization becomes possible.

Free Radical Copolymerization

As preliminary tests showed, the homopolymerization of dyes **9** and **12** with a radical initiator such as azobisisobutyronitrile (AIBN) appeared to be inhibited. However, under the same conditions (2% AIBN, benzene, 70 °C, 30 h), copolymer **25** of dye **12** with 1-vinylpyrrolidone (VP) (monomer molar ratio **12**:VP = 1:9) was obtained in 10% yield (Scheme 11).

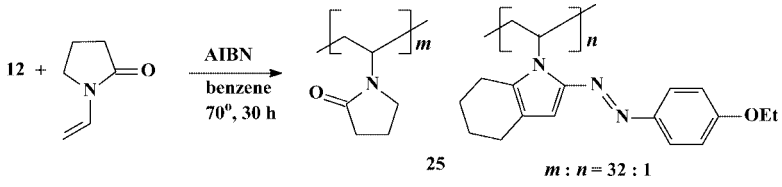
According to the elemental composition, copolymer **25** consists of 3 mol-% of dye **12**. It forms bright yellow solutions in acetone, ethanol, and chloroform, while solutions in dioxane, DMSO, and acetonitrile are red. At a lower content of dye **12** in the monomer mixture (1 mol%), a colored (bright yellow in solution) water-soluble copolymer is formed in 17% yield.

The ability of the synthesized dyes to be copolymerized with common monomers opens an opportunity for the fabrication of intrinsically colored materials, which, when cross-linked, will not fade under the action of solvents or washing. Additionally, the water-solubility of polymer chromogenic azo reagents is known[30] to be important for spectroscopic determination of trace metals in water.

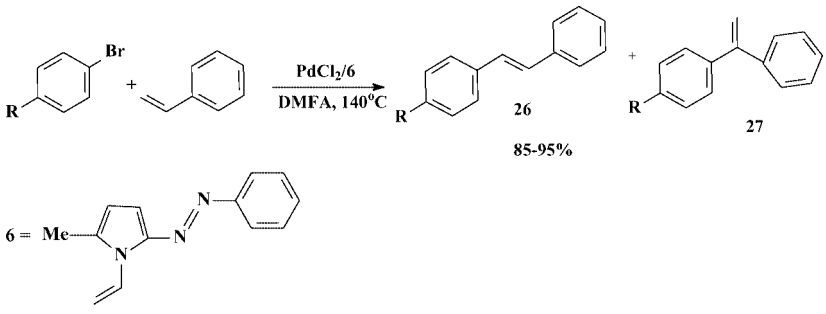
Ligands for Pd Complex Catalysis

Inspired by the work[31] where polymer-tethered azo dyes were used in the design of recoverable Pd catalysts for the Heck reaction, we decided to evaluate the ability of 2-arylazo-1-vinylpyrroles **3**–**22** to serve the same purpose. The presence of the polymerizable *N*-vinyl group (see above) as well as the intrinsically electron-rich pyrrole ring in these molecules, makes cyclopalladation possible and may open up additional possibilities for the development of recoverable polymer-supported transition-metal catalysts based on these molecules. In our preliminary studies we assayed the activity of a Pd complex generated in situ from $PdCl_2$ and 2-methyl-5-phenylazo-1-vinylpyrrole (**6**) in catalysis of the Heck reaction. The reactants (arylbromides and styrene) were treated in the presence of $PdCl_2$ and phenylazopyrrole **6** in DMF (AcONa, HCOONa, Me_4NBr, 140 °C, 1 h, Scheme 12). In the reaction mixture, apart from the major products, *E*-stilbenes **26**, their minor regioisomers, 1,1-diarylethenes **27** (yields up to 5%), have been detected (GLC).

As can be seen from Table 4, the $PdCl_2$/**6** catalytic system allows for a nearly quantitative conversion (90–100%) of arylbromides, including those which are commonly less reactive in the Heck reaction (R = Me, OMe), and high yield of the resulting stilbenes **26** (85–95%) can be obtained, whereas without ligand **6** the conversions and yields are about four times less. Unlike organic tertiary phosphanes



Scheme 11. Copolymerization of dye **12** with 1-vinylpyrrolidone.



Scheme 12. Arylation of styrene with the $PdCl_2$/**6** catalyst (R and corresponding yields are given in Table 4.).

commonly employed as ligands for Pd-based catalysts, the arylazopyrroles are stable in air, allowing for arylations without an inert atmosphere. Furthermore, the presence of the polymerizable *N*-vinyl group may appear useful in the design of recoverable catalysts for such processes.

Table 4. Arylation of styrene with arylbromides in the presence of the $PdCl_2$/**6** catalytic system.

R	Conversion of 4-RC_6H_4Br [%]	Yield of **26** [%]
H	25[a,b]	23[b]
H	100	95
Me	90	85
OMe	90	85
Ac	100	90

[a] GLC-based yields. [b] Without ligand **6**.

Conclusions

In conclusion, a general efficient approach to the synthesis of a novel promising family of reactive azo dyes, namely 2-arylazo-1-vinylpyrroles, has been developed. The approach is based on the low temperature azo coupling of 1-vinylpyrroles, readily available from ketones and acetylene by the Trofimov reaction,[19] with arenediazonium salts in a neutral medium.

Because of the push–pull character and the high polarizability with noncentrosymmetric charge distribution of the synthesized dyes, their UV/Vis spectra are highly responsive to the substituent effects. These results indicate that the dyes can act as tunable chromophores and serve as prospective building blocks for second-order NLO materials.

The potential multifacet isomerism of the dyes (the possible $E \rightleftharpoons Z$ configuration transition of the azo group along with the *syn*⇌*anti* conformational reversible interconversions of the π-conjugated structural units) may appear useful in the design of novel molecular switches, and memory and recording devices.

Strong chromogenic response of the dyes to protonation and complexing secures the potential for the development of new acid-base and metal sensors.

The polymerizability of the dyes paves the way to intrinsically colored polymer materials capable of a reversible color change under the action of light, heat, or chemicals.

Finally, the 2-arylazo-vinylpyrroles synthesized demonstrate the ability to act as robust active ligands in Pd-catalyzed cross-coupling reactions.

Experimental Section

General: ^{1}H- and ^{13}C NMR spectra were recorded with a Bruker DPX 400 spectrometer, HMDS as an internal standard. In order to attribute ^{1}H and ^{13}C peaks 2D homonuclear COSY and NOESY routines, as well as 2D heteronuclear HSQC and HMBC techniques were used. IR spectra were recorded with a Bruker IFS 25 spectrometer in KBr pellets. Spectrophotometric measurements were carried out with a Perkin–Elmer UV/Vis spectrometer Lambda 35.

Geometrical optimizations were performed with GAMESS code,[32] at the DFT-B3LYP level; Becke's three-parameter hybrid functional[33] where non local correlation is provided by Lee, Yang, and Parr correlation functional[34] with the 6-311G* basis set of Pople and coworkers.[35] In all calculations no symmetry constraints were applied as the C_1 symmetry point group was assumed throughout.

The X-ray diffraction data were collected with an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo-K_α radiation at room temperature ($\omega/2\theta$ scanning). The crystalline structure was solved by direct methods and Fourier synthesis (SHELXL-97).[36] Non-hydrogen atoms were refined anisotropically by full-matrix procedure on F^2 with the SHELXL-97 package.[36] Hydrogen atoms were found experimentally and refined isotropically.

CCDC-270103 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The starting 1-vinylpyrroles **2** were prepared by the Trofimov reaction, aromatic amines were of commercial grade.

General Procedure for the Synthesis of 2-Arylazo-1-vinylpyrroles 3–22: A 0 °C solution of the aromatic amine (10 mmol) and aqueous HCl (3 mL) in water 15 (mL) was treated with a 0 °C solution of $NaNO_2$ (0.69 g, 10 mmol) in water (10 mL), and the mixture was stirred at 0 °C for 0.5 h. The resulting diazonium salt solution was neutralized (pH ≈ 7) with dry $NaHCO_3$ (3.0 g, 36 mmol). After stirring for 10 min the solution obtained was poured into a 0 °C solution of 1-vinylpyrrole (10 mmol) in ethanol (10 mL). The mixture was stirred at 0 °C for 2 h. The precipitate was filtered off and dried in vacuo. When no precipitate was formed the reaction mixture was extracted with Et_2O (15 × 3 mL). The extract was dried with K_2CO_3 and distilled off. The products were purified by column chromatography (Al_2O_3, eluent *n*-hexane) or recrystallization from *n*-hexane.

Upon storage of the azo coupling products **3**–**22** at ambient temperature for several months neither change in their UV/Vis spectra nor appearance of foreign signals in their ^{1}H NMR spectra were observed, which provides evidence of their stability.

2-Phenylazo-1-vinylpyrrole 3: Yield: 1.58 g (80%), crimson crystals, m.p. 72–74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (m, 2 H, H_o), 7.87 (dd, $^3J_{B-X}$ = 16.0 Hz, $^3J_{A-X}$ = 8.8 Hz, 1 H, H_X), 7.52 (m, 2 H, H_m), 7.43 (m, 1 H, H_p), 7.36 (m, 1 H, 5-H), 6.79 (m, 1 H, 3-H), 6.45 (m, 1 H, 4-H), 5.38 (d, 1 H, H_B), 4.97 (d, 1 H, H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.46 (C_i), 145.73 (C-2), 129.97 (C_p), 129.84 (C_α), 129.07 (C_m), 122.33 (C_o), 120.73 (C-5), 112.14 (C-4), 100.03 (C-3), 99.66 (C_β) ppm. IR (KBr): $\tilde{\nu}$ = 3165–3105, 1630, 1535, 1501, 1475, 1450, 1410, 1360, 1345, 1305, 1280, 1230, 1180, 1125, 1045, 1005, 955, 905, 880, 800, 765, 710, 675, 650, 580, 550, 500, 450 cm^{-1}. $C_{12}H_{11}N_3$ (197.23): calcd. C 73.07, H 5.62, N 21.30; found C 73.24, H 5.70, N 21.17.

2-(4-Ethoxyphenylazo)-1-vinylpyrrole 4: Yield: 1.25 g (52%), dark-red crystals, m.p. 72–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, $^3J_{o-m}$ = 8.8 Hz, 2 H, H_m), 7.83 (dd, $^3J_{B-X}$ = 16.1 Hz, $^3J_{A-X}$ = 8.8 Hz, 1 H, H_X), 7.29 (m, 1 H, 5-H), 7.00 (m, 2 H, H_o), 6.70 (m, 1 H, 3-H), 6.41 (m, 1 H, 4-H), 5.33 (d, 1 H, H_B), 4.91 (d, 1 H, H_A), 4.14 (q, 2 H, CH_2Me, $^3J_{CH_2-Me}$ = 6.9 Hz), 1.48 (t, 3 H, CH_2Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.72 (C_p), 147.69 (C_i), 145.72 (C-2), 129.94 (C_α), 124.02 (C_o), 119.78 (C-5), 114.72 (C_m), 111.86 (C-4), 99.14 (C-3), 99.08 (C_β), 63.82 (CH_2Me), 14.86 (CH_2Me) ppm. IR (KBr), $\tilde{\nu}$ = 2975, 2930, 1640, 1590, 1580, 1595, 1475, 1405, 1350, 1310, 1290, 1250, 1130, 1100, 1060, 1030,

955, 905, 875, 820, 800, 710, 660, 625, 575, 550, 545, 515, 475 cm^{-1}. $C_{14}H_{15}N_3O$ (241.29): calcd. C 69.69, H 6.27, N 17.41; found C 70.01, H 6.38, N 17.57.

2-(4-Nitrophenylazo)-1-vinylpyrrole 5: Yield: 2.03 g (84%), orange crystals, m.p. 176–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, $^3J_{o-m}$ = 8.9 Hz, 2 H, H_m), 7.95 (m, 2 H, H_o), 7.80 (dd, $^3J_{B-X}$ = 16.1 Hz, $^3J_{A-X}$ = 8.7 Hz, 1 H, H_X), 7.48 (m, 1 H, 5-H), 6.90 (m, 1 H, 5 H), 6.51 (m, 1 H, 4-H), 5.45 (d, 1 H, H_B), 5.06 (d, 1 H, H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.09 (C_i), 147.74 (C_p), 146.23 (C-2), 129.54 (C_α), 124.84 (C_m), 123.35 (C-5), 122.70 (C_o), 113.19 (C-4), 102.55 (C-3), 101.08 (C_β) ppm. IR (KBr) $\tilde{\nu}$ = 3110, 3090, 1640, 1600, 1575, 1505, 1460, 1370, 1350, 1325, 1255, 1180, 1130, 1100, 1065, 1110, 960, 870, 845, 750, 745, 685, 650, 605, 590, 500, 455 cm^{-1}. $C_{12}H_{10}N_4O_2$ (242.24): calcd. C 59.50, H 4.16, N 23.13; found C 59.52, H 4.24, N 22.87.

5-Methyl-2-phenylazo-1-vinylpyrrole 6: Yield: 1.69 g (80%), brick-red crystals, m.p. 52–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, $^3J_{o-m}$ = 7.5 Hz, 2 H, H_o), 7.42 (m, 2 H, H_m), 7.34 (dd, $^3J_{B-X}$ = 16.2 Hz, $^3J_{A-X}$ = 8.8 Hz, 1 H, H_X), 7.32 (m, 1 H, H_p), 6.71 (d, $^3J_{3-4}$ = 4.1 Hz, 1 H, 3-H), 6.12 (d, 1 H, 4-H), 5.43 (d, 1 H, H_B), 5.17 (d, 1 H, H_A), 2.42 (s, 3 H, *Me*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.78 (C_i), 147.11 (C-2), 134.79 (C-5), 129.22 (C_p), 129.22 (C_α), 128.99 (C_m), 122.15 (C_o), 111.66 (C-4), 107.72 (C_β), 99.87 (C-3), 14.47 (*Me*) ppm. IR (KBr) $\tilde{\nu}$ = 3056, 2981, 2975, 2955, 2920, 2910, 1638, 1538, 1480, 1452, 1433, 1411, 1384, 1348, 1331, 1291, 1186, 1150, 1082, 1072, 1030, 1017, 993, 978, 919, 906, 884, 862, 840, 772, 692, 675, 636, 613, 577, 556, 514 cm^{-1}. $C_{13}H_{13}N_3$ (211.26): calcd. C 73.91, H 6.20, N 19.89; found C 73.66, H 6.34, N 19.46.

2-(4-Ethoxyphenylazo)-5-methyl-1-vinylpyrrole 7: Yield: 1.94 g (76%), brick-red powder, m.p. 74–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, $^3J_{o-m}$ = 8.8 Hz, 2 H, H_o), 7.33 (dd, $^3J_{B-X}$ = 16.1 Hz, $^3J_{A-X}$ = 9.3 Hz, 1 H, H_X), 6.92 (d, 2 H, H_m), 6.62 (d, $^3J_{3-4}$ = 3.9 Hz, 1 H, 3-H), 6.07 (d, 1 H, 4-H), 5.40 (d, 1 H, H_B), 5.12 (d, 1 H, H_A), 4.07 (q, $^3J_{CH_2-Me}$ = 6.9 Hz, 2 H, CH_2Me), 2.40 (s, 3 H, Me_{Py}), 1.42 (t, 3 H, CH_2Me) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 160.19 (C_p), 147.64 (C_i), 146.06 (C-2), 133.77 (C-5), 129.78 (C_α), 123.74 (C_o), 114.71 (C_m), 111.30 (C-4), 107.06 (C_β), 98.80 (C-3), 63.78 (CH_2Me), 14.88 (CH_2Me), 14.53 (Me_{Py}) ppm. IR (KBr): $\tilde{\nu}$ = 3122, 3076, 2974, 2938, 1642, 1598, 1578, 1499, 1474, 1428, 1409, 1393, 1371, 1352, 1326, 1299, 1252, 1187, 1149, 1114, 1081, 1042, 1024, 967, 921, 879, 840, 803, 773, 669, 635, 576, 556, 531, 462 cm^{-1}. $C_{15}H_{17}N_3O$ (255.31): calcd. C 70.56, H 6.71, N 16.46; found C 71.01, H 6.80, N 16.46.

5-Methyl-2-(4-nitrophenylazo)-1-vinylpyrrole 8: Yield: 2.18 g (85%), red crystals, m.p. 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, $^3J_{o-m}$ = 9.0 Hz, 2 H, H_m), 7.81 (d, 2 H, H_o), 7.29 (dd, $^3J_{B-X}$ = 15.9 Hz, $^3J_{A-X}$ = 9.3 Hz, 1 H, H_X), 6.84 (d, $^3J_{3-4}$ = 4.2 Hz, 1 H, 3-H), 6.21 (d, 1 H, 4-H), 5.44 (d, 1 H, H_B), 5.29 (d, 1 H, H_A), 2.45 (s, 3 H, *Me*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.58 (C_i), 147.64 (C-2), 147.06 (C_p), 138.21 (C-5), 129.27 (C_α), 124.78 (C_m), 122.34 (C_o), 113.33 (C-4), 109.54 (C_β), 102.70 (C-3), 14.60 (*Me*) ppm. IR (KBr): $\tilde{\nu}$ = 3122, 3095, 2995, 2958, 2913, 1643, 1603, 1585, 1517, 1472, 1432, 1391, 1367, 1335, 1297, 1179, 1149, 1104, 1076, 1035, 997, 894, 781, 753, 691, 620, 507, 458 cm^{-1}. $C_{13}H_{12}N_4O_2$ (256.26): calcd. C 60.93, H 4.72, N 21.86; found C 60.56, H 4.54, N 21.68.

2-(4-Bromophenylazo)-5-methyl-1-vinylpyrrole 9: Yield: 2.21 g (76%), orange needles, m.p. 72–74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, $^3J_{o-m}$ = 8.8 Hz, 2 H, H_o), 7.53 (d, 2 H, H_m), 7.31 (dd, $^3J_{B-X}$ = 16.1 Hz, $^3J_{A-X}$ = 9.3 Hz, 1 H, H_X), 6.71 (d, $^3J_{3-4}$ = 3.9 Hz, 1 H, 3-H), 6.13 (d, 1 H, 4-H), 5.40 (d, 1 H, H_B), 5.16 (d, 1 H, H_A), 2.41 (s, 3 H, *Me*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.57 (C_i), 147.01 (C-2), 135.53 (C-5), 132.16 (C_m), 129.55 (C_α), 123.58 (C_o), 123.01 (C_p), 112.09 (C-4), 108.17 (C_β), 100.93 (C-3), 14.55 (*Me*) ppm. IR (KBr): $\tilde{\nu}$ = 3127, 3055, 2911, 1643, 1582, 1567, 1535, 1474, 1433, 1416, 1388, 1344, 1303, 1293, 1206, 1182, 1150, 1062, 1026, 1004, 960, 886, 831, 812, 783, 774, 762, 706, 510, 492, 458 cm^{-1}. $C_{13}H_{12}BrN_3$ (290.16): calcd. C 53.81, H 4.17, Br 27.54, N 14.48; found C 53.97, H 4.09, Br 27.51, N 14.33.

5-Methyl-2-(4-phenylazophenylazo)-1-vinylpyrrole 10: Yield: 2.48 g (79%), vinous crystals, m.p. 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, $^3J_{o-m}$ = 8.3 Hz, 2 H, H_o), 7.92 (d, $^3J_{o'-m'}$ = 7.6 Hz, 2 H, $H_{o'}$), 7.89 (d, 2 H, H_m), 7.50 (m, 2 H, $H_{m'}$), 7.47 (m, 2 H, $H_{p'}$), 7.35 (dd, $^3J_{B-X}$ = 16.2 Hz, $^3J_{A-X}$ = 9.3 Hz, 1 H, H_X), 6.77 (d, $^3J_{3-4}$ = 3.4 Hz, 1 H, 3-H), 6.16 (d, 1 H, 4-H), 5.45 (d, 1 H, H_B), 5.22 (d, 1 H, H_A), 2.43 (s, 3 H, *Me*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.33 (C_i), 152.90 ($C_{i'}$), 152.53 (C_p), 147.59 (C-2), 136.13 (C-5), 131.12 ($C_{p'}$), 129.56 (C_α), 129.18 ($C_{m'}$), 123.91 (C_o), 123.00 ($C_{o'}$), 122.90 (C_m), 112.43 (C-4), 108.35 (C_β), 100.93 (C-3), 14.61 (*Me*) ppm. IR (KBr): $\tilde{\nu}$ = 3095, 3031, 2939, 1640, 1474, 1430, 1411, 1388, 1364, 1343, 1291, 1224, 1179, 1126, 1080, 1071, 1031, 972, 880, 859, 786, 771, 689, 628, 553, 529, 452 cm^{-1}. $C_{19}H_{17}N_5$ (315.37): calcd. C 72.36, H 5.43, N 22.21; found C 72.25, H 5.43, N 21.28.

2-Phenylazo-1-vinyl-4,5,6,7-tetrahydroindole 11: Yield: 2.19 g (87%), brick-red crystals, m.p. 62–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, $^3J_{o-m}$ = 8.0, Hz 2 H, H_o), 7.47 (dd, $^3J_{B-X}$ = 16.1 Hz, $^3J_{A-X}$ 9.3 =Hz, 1 H, H_X), 7.42 (m, 2 H, H_m), 7.31 (m, 1 H, H_p), 6.57 (s, 1 H, 3 H), 5.31 (d, 1 H, H_B), 5.00 (d, 1 H, H_A), 2.78 (t, $^3J_{6-7}$ = 6.1 Hz, 2 H, 7-H), 2.56 (t, $^3J_{4-5}$ = 6.1 Hz, 2 H, 4-H), 1.85 (m, 2 H, 6-H), 1.75 (m, 2 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.91 (C_i), 146.14 (C-2), 134.71 (C-8), 129.43 (C_α), 129.01 (C_m), 129.01 (C_p), 122.66 (C-9), 122.09 (C_o), 104.54 (C_β), 98.97 (C-3), 24.60 (C-7), 23.20 (C-4), 23.20 (C-6), 22.86 (C-5) ppm. IR (KBr): $\tilde{\nu}$ = 2937, 2835, 1640, 1473, 1447, 1432, 1412, 1360, 1338, 1323, 1291, 1261, 1242, 1199, 1137, 1094, 1069, 971, 952, 911, 868, 830, 807, 765, 719, 690, 633, 558, 514 486, 454 cm^{-1}. $C_{16}H_{17}N_3$ (251.33): calcd. C 76.46, H 6.82, N 16.72; found C 76.38, H 6.87, N 16.35.

2-(4-Ethoxyphenylazo)-1-vinyl-4,5,6,7-tetrahydroindole 12: Yield: 2.36 g (80%), red crystals, m.p. 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, $^3J_{o-m}$ = 8.2 Hz, 2 H, H_m), 7.47 (dd, $^3J_{B-X}$ = 16.3 Hz, $^3J_{A-X}$ 9.2 Hz, 1 H, H_X), 6.93 (d, 2 H, H_o), 6.49 (s, 1 H, 3-H), 5.30 (d, 1 H, H_B), 4.97 (d, 1 H, H_A), 4.08 (q, $^3J_{CH_2-Me}$ = 6.7 Hz, 2 H, CH_2Me), 2.78 (t, $^3J_{6-7}$ = 5.7 Hz, 2 H, 7-H), 2.55 (t, $^3J_{4-5}$ = 5.7 Hz, 2 H, 4-H), 1.85 (m, 2 H, 6-H), 1.75 (m, 2 H, 5-H), 1.43 (t, 3 H, CH_2Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.02 (C_p), 148.11 (C_i), 146.04 (C-2), 133.48 (C-8), 129.55 (C_α), 123.64 (C_o), 122.20 (C-9), 114.71 (C_m), 103.87 (C_β), 98.02 (C-3), 63.79 (CH_2Me), 24.56 (C-7), 23.27 (C-4), 23.17 (C-6), 22.91 (C-5), 14.90 (CH_2Me) ppm. IR (KBr): $\tilde{\nu}$ = 2975, 2932, 2857, 1642, 1598, 1578, 1556, 1496, 1468, 1422, 1406, 1390, 1366, 1329, 1310, 1297, 1243, 1164, 1141, 1126, 1096, 1076, 1045, 1020, 956, 921, 887, 840, 824, 807, 790, 687, 633, 573, 563, 533 cm^{-1}. $C_{18}H_{21}N_3O$ (295.38): calcd. C 73.19, H 7.17, N 14.23; found C 73.15, H 7.47, N 14.06.

2-(4-Nitrophenylazo)-1-vinyl-4,5,6,7-tetrahydroindole 13: Yield: 2.78 g (94%), vinous crystals, m.p. 150–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, $^3J_{o-m}$ = 8.6 Hz, 2 H, H_m), 7.80 (d, 2 H, H_o), 7.41 (dd, $^3J_{B-X}$ = 16.1 Hz, $^3J_{A-X}$ = 9.0 Hz, 1 H, H_X), 6.70 (s, 1 H, 3-H), 5.36 (d, 1 H, H_B), 5.13 (d, 1 H, H_A), 2.81 (m, 2 H, 7-H), 2.58 (m, 2 H, 4-H), 1.88 (m, 2 H, 6-H), 1.78 (m, 2-H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.86 (C_i), 146.84

(C_p), 146.84 (C-2), 138.58 (C-8), 128.98 (C_α), 124.82 (C_m), 124.51 (C-9), 122.22 (C_o), 106.43 (C_β), 101.56 (C-3), 24.77 (C-7), 23.10 (C-4), 22.95 (C-6), 22.68 (C-5) ppm. IR (KBr): $\tilde{\nu}$ = 3104, 2937, 2857, 1639, 1603, 1585, 1511, 1466, 1410, 1326, 1312, 1294, 1283, 1220, 1197, 1133, 1104, 1073, 1016, 884, 851, 752, 687, 668, 613, 542, 498 cm^{-1}. $C_{16}H_{16}N_4O_2$ (296.32): calcd. C 64.85, H 5.44, N 18.91; found C 65.04, H 5.85, N 18.68.

2-(4-Bromophenylazo)-1-vinyl-4,5,6,7-tetrahydroindole 14: Yield: 2.71 g (82%), brick-red crystals, m.p. 78–79 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, $^3J_{o-m}$ = 8.6 Hz, 2 H, H_o), 7.52 (d, 2 H, H_m), 7.42 (dd, $^3J_{B-X}$ = 16.1 Hz, $^3J_{A-X}$ = 9.3 Hz, 1 H, H_X), 6.58 (s, 1 H, 3-H), 5.30 (d, 1 H, H_B), 5.02 (d, 1 H, H_A), 2.77 (t, $^3J_{6-7}$ = 5.9 Hz, 2 H, 7-H), 2.55 (t, $^3J_{4-5}$ = 6.1 Hz, 2 H, 4-H), 1.86 (m, 2 H, 6-H), 1.75 (m, 2 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.70 (C_i), 146.06 (C-2), 135.47 (C-8), 132.08 (C_m), 129.24 (C_α), 123.78 (C_o), 123.04 (C-9), 122.64 (C_p), 104.89 (C_β), 99.59 (C-3), 24.59 (C-7), 23.10 (C-4), 23.10 (C-6), 22.77 (C-5) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2855, 1642, 1468, 1412, 1363, 1337, 1323, 1288, 1197, 1136, 1095, 1064, 1000, 959, 889, 834, 739, 705, 629, 601, 587, 511, 484, 460 cm^{-1}. $C_{16}H_{16}BrN_3$ (330.23): calcd. C 58.20, H 4.88, Br 24.20, N 12.72; found C 58.18, H 4.87, Br 24.31, N 12.74.

2-(4-Phenylazophenylazo)-1-vinyl-4,5,6,7-tetrahydroindole 15: Yield: 2.88 g (81%), green powder, m.p. 98–100 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, $^3J_{o-m}$ = 8.8 Hz, 2 H, H_o), 7.92 (d, $^3J_{o'-m'}$ = 7.1 Hz, 2 H, $H_{o'}$), 7.87 (d, 2 H, H_m), 7.51 (m, 2 H, $H_{m'}$), 7.48 (dd, $^3J_{B-X}$ = 16.2 Hz, $^3J_{A-X}$ = 9.5 Hz, 1 H, H_X), 7.46 (m, 1 H, $H_{p'}$), 6.65 (s, 1 H, 3-H), 5.34 (d, 1 H, H_B), 5.07 (d, 1 H, H_A), 2.80 (t, $^3J_{6-7}$ = 5.9 Hz, 2 H, 7-H), 2.57 (t, $^3J_{4-5}$ = 6.1 Hz, 2 H, 4-H), 1.86 (m, 2 H, 6-H), 1.77 (m, 2 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.33 (C_i), 152.93 ($C_{i'}$), 152.35 (C_p), 146.70 (C-2), 136.19 (C-8), 131.02 ($C_{p'}$), 129.27 (C_α), 129.14 ($C_{m'}$), 123.91 (C_o), 123.43 (C-9), 122.77 ($C_{o'}$), 122.96 (C_m), 105.17 (C_β), 99.97 (C-3), 24.67 (C-7), 23.12 (C-4), 23.09 (C-6), 22.77 (C-5) ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2932, 2853, 1640, 1597, 1504, 1471, 1436, 1408, 1362, 1333, 1323, 1311, 1287, 1222, 1200, 1138, 1124, 1093, 1073, 1058, 1019, 854, 834, 813, 764, 684, 627, 550, 527 cm^{-1}. $C_{22}H_{21}N_5$ (355.44): calcd. C 74.34, H 5.96, N 19.70; found C 74.80 H 6.03, N 19.31.

5-Phenyl-2-phenylazo-1-vinylpyrrole 16: Yield: 1.45 g (53%), red crystals, m.p. 72–74 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, $^3J_{o-m}$ = 8.1 Hz, 2 H, H_o), 7.53 (d, $^3J_{o'-m'}$ = 7.7 Hz, 2 H, $H_{o'}$), 7.45 (m, 2 H, H_m), 7.45 (m, 2 H, $H_{m'}$), 7.39 (m, 1 H, H_p), 7.39 (m, 1 H, $H_{p'}$), 7.22 (dd, $^3J_{B-X}$ = 16.0 Hz, $^3J_{A-X}$ = 9.2 Hz, 1 H, H_X), 6.92 (d, $^3J_{3-4}$ = 4.2 Hz, 1 H, 3-H), 6.44 (d, 1 H, 4-H), 5.42 (d, 1 H, H_B), 5.19 (d, 1 H, H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.78 (C_i), 148.33 (C-2), 138.41 (C-5), 132.10 ($C_{i'}$), 129.87 (C_α), 129.64 (C_p), 129.14 ($C_{o'}$), 129.08 (C_m), 128.44 ($C_{m'}$), 128.00 ($C_{p'}$), 122.38 (C_o), 112.68 (C-4), 110.36 (C_β), 100.38 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3111, 3061, 3027, 2860, 1641, 1600, 1533, 1496, 1465, 1449, 1418, 1392, 1351, 1298, 1278, 1234, 1154, 1072, 1040, 999, 962, 895, 760, 690, 658, 561, 512 cm^{-1}. $C_{18}H_{15}N_3$ (273.34): calcd. C 79.10, H 5.53, N 17.37; found C 79.38, H 5.87, N 17.14.

2-(4-Nitrophenylazo)-5-phenyl-1-vinylpyrrole 17: Yield: 1.78 g (56%), orange crystals, m.p. 140–144 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, $^3J_{o-m}$ = 9.0 Hz, 2 H, H_m), 7.92 (d, 2 H, H_o), 7.58 (m, 2 H, $H_{o'}$), 7.48 (m, 2 H, $H_{m'}$), 7.39 (m, 1 H, $H_{p'}$), 7.24 (dd, $^3J_{B-X}$ = 15.9 Hz, $^3J_{A-X}$ = 9.0 Hz, 1 H, H_X), 7.05 (d, 1 H, 3-H), 6.55 (d, 1 H, 4-H), 5.45 (d, 1 H, H_B), 5.30 (d, 1 H, H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.48 (C_i), 148.88 (C-2), 147.36 (C_p), 141.11 (C-5), 132.48 ($C_{i'}$), 129.63 (C_α), 129.36 ($C_{o'}$), 128.74 ($C_{m'}$), 128.66 ($C_{p'}$), 124.87 (C_m), 122.62 (C_o), 113.89 (C-4), 111.84 (C_β), 102.88 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 1625, 1600, 1575, 1500, 1450, 1410, 1380, 1310, 1305, 1295, 1180, 1145, 1095, 1035, 1000, 905, 895, 855, 840, 875, 750, 710, 700, 690, 650, 530, 490 cm^{-1}. $C_{18}H_{14}N_4O_2$ (318.33): calcd. C 67.92, H 4.43, N 17.60; found C 67.92, H 4.48, N 17.37.

5-(4-Methoxyphenyl)-2-phenylazo-1-vinylpyrrole 18: Yield: 1.73 g (57%), red crystals, m.p. 76–78 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, $^3J_{o-m}$ = 8.7 Hz, 2 H, H_o), 7.50 (m, 2 H, H_m), 7.48 (d, $^3J_{o'-m'}$ = 8.7 Hz, 2 H, $H_{m'}$), 7.40 (m, 1 H, H_p), 7.22 (dd, $^3J_{B-X}$ = 15.9 Hz, $^3J_{A-X}$ = 9.0 Hz, 1 H, H_X), 7.01 (m, 2 H, $H_{o'}$), 6.94 (d, $^3J_{3-4}$ = 4.0 Hz, 1 H, 3-H), 6.42 (d, 1 H, 4-H), 5.46 (d, 1 H, H_B), 5.21 (d, 1 H, H_A), 3.90 (s, 3 H, *Me*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.61 ($C_{p'}$), 153.76 (C_i), 148.12 (C-2), 138.60 (C-5), 130.52 ($C_{o'}$), 129.97 (C_α), 129.47 (C_p), 129.08 (C_m), 124.58 ($C_{i'}$), 122.31 (C_o), 114.07 ($C_{m'}$), 112.23 (C-4), 110.09 (C_β), 100.54 (C-3), 55.44 (*Me*) ppm. IR (KBr): $\tilde{\nu}$ = 2996, 2967, 2934, 2836, 1643, 1608, 1573, 1537, 1503, 1464, 1448, 1436,1406, 1390, 1356, 1316, 1298, 1247, 1213, 1178, 1149, 1109, 1069, 1035, 1023, 959, 892, 835, 782, 771, 714, 684, 629, 613, 593, 559, 525, 499, 471 cm^{-1}. $C_{19}H_{17}N_3O$ (303.36): calcd. C 75.23, H 5.65, N 13.85; found C 74.96, H 5.48, N 13.74.

5-(4-Methoxyphenyl)-2-(4-nitrophenylazo)-1-vinylpyrrole 19: Yield: 1.95 g (56%), vinous crystals, m.p. 122–124 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, $^3J_{o-m}$ = 9.0 Hz, 2 H, H_m), 7.80 (d, 2 H, H_o), 7.52 (d, $^3J_{o'-m'}$ = 8.8 Hz, 2 H, $H_{m'}$), 7.17 (dd, $^3J_{B-X}$ = 15.9 Hz, $^3J_{A-X}$ = 9.1 Hz, 1 H, H_X), 7.06 (d, 2 H, $H_{o'}$), 7.03 (d, $^3J_{3-4}$ = 4.3 Hz, 1 H, 3-H), 6.52 (d, 1 H, 4-H), 5.53 (d, 1 H, H_B), 5.37 (d, 1 H, H_A), 3.87 (s, 3 H, *Me*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.04 ($C_{p'}$), 157.55 (C_i), 148.68 (C-2), 147.15 (C_p), 141.44 (C-5), 130.55 ($C_{m'}$), 129.69 (C_α), 124.89 (C_m), 123.76 ($C_{i'}$), 122.49 (C_o), 114.22 ($C_{o'}$), 113.57 (C-4), 111.75 (C_β), 103.06 (C-3), 55.40 (Me) ppm. IR (KBr): $\tilde{\nu}$ = 3114, 2934, 2832, 1642, 160,8 1583, 1535, 151, 1458, 1437, 1417, 1381, 1333, 1286, 1254, 1239, 1188, 1151, 1147, 1105, 1080, 1043, 1024, 970, 916, 899, 832, 810, 783, 753, 718, 691, 656, 627, 518, 528, 507, 467 cm^{-1}. $C_{19}H_{16}N_4O_3$ (348.36): calcd. C 65.51, H 4.63, N 16.08; found C 65.67, H 5.00, N 15.85.

5-Furyl-2-phenylazo-1-vinylpyrrole 20: Yield: 1.40 g (53%), orange crystals, m.p. 86–88 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, $^3J_{o-m}$ = 7.8 Hz, 2 H, H_o), 7.49 (m, 1 H, 5′-H), 7.45 (m, 2 H, H_m), 7.37 (t, $^3J_{p-m}$ = 7.1 Hz, 1 H, H_p), 7.26 (dd, $^3J_{B-X}$ = 15.8 Hz, $^3J_{A-X}$ = 8.8 Hz, 1 H, H_X), 6.87 (br. s, 1 H, 3-H), 6.62 (d, $^3J_{3-4}$ = 4.3 Hz, 1 H, 4-H), 6.58 (m, 1 H, 4′-H), 6.49 (m, 1 H, 3′-H), 5.57 (d, 1 H, H_B), 5.36 (d, 1 H, H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.67 (C_i), 148.18 (C-2), 146.27 (C-2′), 142.64 (C-5′), 129.74 (C_α), 129.74 (C_p), 129.09 (C_m), 128.72 (C-5), 122.40 (C_o), 112.16 (C_β), 111.69 (C-4), 111.59 (C-4′), 109.07 (C-3′), 100.73 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3143, 3123, 3062, 3026, 2926, 1639, 1486, 1479, 1453, 1427, 1390, 1374, 1344, 1327, 1298, 1236, 1217, 1148, 1070, 1057, 1041, 1016, 959, 924, 886, 876, 779, 763, 695, 687, 604, 552, 522, 496 cm^{-1}. $C_{16}H_{13}N_3O$ (263.30): calcd. C 72.99, H 4.98, N 15.96; found C 73.16, H 5.06, N 16.11.

2-Phenylazo-5-thienyl-1-vinylpyrrole 21: Yield: 1.48 g (53%), orange crystals, m.p. 74–76 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, $^3J_{o-m}$ = 7.8 Hz, 2 H, H_o), 7.50 (m, 2 H, H_m), 7.41 (m, 1 H, H_p), 7.40 (m, 1 H, 5′-H), 7.26 (dd, $^3J_{B-X}$ = 15.9 Hz, $^3J_{A-X}$ = 8.9 Hz, 1 H, H_X), 7.26 (m, 1 H, 3′-H), 7.14 (m, 1 H, 4′-H), 6.90 (d, $^3J_{3-4}$ = 4.2 Hz, 1 H, 3-H), 6.55 (d, 1 H, 4-H), 5.62 (d, 1-H, H_B), 5.37 (d, 1 H, H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.10 (C_i), 147.89 (C-2), 133.05 (C-5), 131.12 (C-2′), 129.23 (C_p), 129.08 (C_α), 128.62 (C_m), 127.23 (C-4′), 126.79 (C-3′), 125.95 (C-5′), 121.89 (C_o), 112.60 (C-4), 111.70 (C_β), 100.17 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3122, 3063, 3031, 1634, 1466, 1450, 1435, 1422, 1388, 1344, 1321, 1213,

1193, 1147, 1070, 1057, 1040, 1013, 959, 928, 843, 778, 762, 700, 686, 600, 543, 522, 498 cm^{-1}. $C_{16}H_{13}N_3S$ (279.36): calcd. C 68.79, H 4.69, N 15.04, S 11.48; found: C 69.06, H 4.50, N 15.24, S 11.71.

2-(4-Nitrophenylazo)-5-thienyl-1-vinylpyrrole 22: Yield: 2.56 g (79%), vinous crystals, m.p. 136–140 °C. ^1H NMR (400 MHz, $CDCl_3$): 8.39 δ = (d, $^3J_{o-m}$ = 9.0 Hz, 2 H, H_m), 7.81 (d, 2 H, H_o), 7.50 (d, $^3J_{4'-5'}$ = 4.4 Hz, 1 H, $H_{5'}$), 7.39 (d, $^3J_{3'-4'}$ = 3.5 Hz, 1 H, $H_{3'}$), 7.26 (dd, $^3J_{B-X}$ = 15.7 Hz, $^3J_{A-X}$ = 8.8 Hz, 1 H, H_X), 7.14 (m, 1 H, 4′-H), 7.07 (d, $^3J_{3-4}$ = 4.3 Hz, 1 H, 3-H), 6.68 (d, 1 H, 4-H), 5.68 (d, 1 H, H_B), 5.54 (d, 1 H, H_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.44 (C_i), 148.91 (C-2), 147.38 (C_p), 134.44 (C-5), 132.93 (C-2′), 129.39 (C_α), 127.99 (C-4′), 127.82 (C-3′), 127.26 (C-5′), 124.89 (C_m), 122.62 (C_o), 114.02 (C-4), 114.02 (C_β), 103.16 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3113, 3077, 2958, 2922, 2852, 1640, 1601, 1584, 1512, 1460, 1379, 1330, 1304, 1196, 1172, 1151, 1101, 1038, 851, 770, 753, 694 cm^{-1}. $C_{16}H_{12}N_4O_2S$ (324.36): calcd. C 59.25, H 3.73, N 17.27, S 9.88; found C 59.59, H 4.01, N 17.00, S 9.69.

Protonation of Azopyrrole 9: An orange solution of azopyrrole **9** (10 mg, 0.034 mmol) in $CDCl_3$ (1 mL) was added to CF_3COOH (4 mg, 0.035 mmol). The reaction mixture became red-brown. After recording the spectrum [^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, $^3J_{3-4}$ = 3.9 Hz, 1 H, 3-H), 7.59 (d, $^3J_{o-m}$ = 8.8 Hz, 2 H, H_o), 7.47 (d, 2 H, H_m), 7.00 (dd, $^3J_{B-X}$ = 16.1 Hz $^3J_{A-X}$ = 9.3 Hz, 1 H, H_X), 6.86 (d, 1 H, 4-H), 5.82 (d, 1 H, H_A), 5.68 (d, 1 H, H_B), 2.61 (s, 3 H, *Me*) ppm], the solution was mixed with $NaHCO_3$ (9 mg) at room temperature and then filtered. The initial color was completely restored, and the ^1H NMR, spectrum corresponded to that of initial compound **9**. Protonation of azopyrrole **12** was carried out analogously.

Complexing of Azopyrrole 12 with BF_3·OEt_2: A solution of azopyrrole **12** (6 mg, 0.020 mmol) in $CDCl_3$ (1 mL) was added to BF_3·OEt_2 (3 mg, 0.021 mmol) whilst stirring at room temperature. The reaction mixture became red-brown. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, $^3J_{o-m}$ = 8.2 Hz, 2 H, H_m), 7.59 (s, 1 H, 3-H), 7.13 (dd, $^3J_{B-X}$ = 16.3 Hz, $^3J_{A-X}$ = 9.2 Hz, 1 H, H_X), 6.89 (d, 2 H, H_o), 5.46 (d, 1 H, H_B), 5.38 (d, 1 H, H_A), 4.05 (q, $^3J_{CH_2-Me}$ = 8.2 Hz, 2 H, CH_2Me), 2.81 (t, $^3J_{6-7}$ = 5.7 Hz, 2 H, 7-H), 2.60 (t, $^3J_{4-5}$ = 5.7 Hz, 2 H, 4-H), 1.85 (m, 2 H, 6-H), 1.75 (m, 2 H, 5-H), 1.43 (t, 3 H, CH_2*Me*) ppm.

A solution of azopyrrole **12** (6 mg, 0.020 mmol) in benzene (10 mL) was added to BF_3·OEt_2 (3 mg, 0.021 mmol) whilst stirring at room temperature. The violet solution prepared was diluted with benzene to 2×10^{-4} mol L^{-1} to record the UV/Vis spectrum.

Copolymerization of the Azopyrrole 12 with 1-Vinylpyrrolidone (VP): A solution of pyrrole **12** (23 mg, 0.078 mmol), VP (77 mg, 0.694 mmol), and AIBN (2 mg, 2%) in benzene (0.1 mL) was placed in a glass ampule under argon. The ampule was sealed and kept at 70 °C for 30 h. The copolymer was purified by reprecipitation from the benzene solution to *n*-hexane and washed with Et_2O to give 10 mg of a brown powder (yield 10%). IR (KBr): $\tilde{\nu}$ = 2950, 2905, 2860, 1680, 1620, 1590, 1570, 1495, 1470, 1420, 1380, 1280, 1220, 1100, 1020, 960, 910, 820 cm^{-1}. **25**: $C_{210}H_{309}N_{35}O_{33}$ (3851.98): calcd. C 65.45, H 8.10, N 12.72; found C 66.28, H 7.98, N 12.87.

Arylation of Styrene: A mixture of arylbromide (10.00 mmol), styrene (1040 mg, 10.00 mmol), $PdCl_2$ (28 mg, 0.16 mmol), AcONa (905 mg, 11.00 mmol), HCOONa (136 mg, 2.00 mmol), NMe_4Br (246 mg, 1.60 mmol), and azopyrrole **6** (68 mg, 0.32 mmol) in dry DMF (10 mL) was stirred at 140 °C for 1 h, and then analyzed by GLC.

Acknowledgments

This work was supported by the Russian Science Support Foundation, President grant (MK-1707.2005.3) and the Presidium of the Russian Academy of Sciences (grant No. 10002-251/P-25/155-305/200404-072).

[1] N. Yokomichi, K. Seki, S. Tada, T. Yamabe, *Synth. Met.* **1995**, *69*, 577–578.
[2] G. Zotti, S. Zecchin, G. Schiavon, A. Berlin, G. Pagani, A. Canavesi, G. Casalbore-Miceli, *Synth. Met.* **1996**, *78*, 51–57.
[3] A. Chyla, S. Kucharski, J. Sworakowski, M. Bieńkovski, *Thin Solid Films* **1996**, *284–285*, 496–499.
[4] J. D. Nero, D. Laks, *Synth. Met.* **1999**, *101*, 440–441.
[5] Y. Ishida, Y. Murata, JP 06145544, **1994** [*Chem. Abstr.* **1994**, *121*, 282311].
[6] T. Kawafuoni, N. Yanagihara, Y. Shinjo (Ricoh Co., Ltd., Japan), JP 2002129049, **2002** [*Chem. Abstr.* **2002**, *136*, 18109].
[7] Y. Ueno, T. Sato, T. Tomura, T. Noguchi (Ricoh Co., Ltd., Japan), JP 20022883731, **2002** [*Chem. Abstr.* **2002**, *137*, 286541].
[8] Y. Ueno (Ricoh Co., Ltd., Japan), JP 20022347348, **2003** [*Chem. Abstr.* **2003**, *138*, 18109].
[9] Z. Zhu, Y. Wang, Y. Lu, *Macromolecules* **2003**, *36*, 9585–9593.
[10] E. Wagner-Wysiecka, E. Luboch, M. Kowalczyk, J. F. Biernat, *Tetrahedron* **2003**, *59*, 4415–4420.
[11] A. Facchetti, A. Abbotti, L. Beverina, M. E. van der Boom, P. Dutta, G. Evmenenko, T. J. Marks, G. A. Pagani, *Chem. Mater.* **2002**, *14*, 4996–5005.
[12] Y. Wang, J. Ma, Y. Jiang, *J. Phys. Chem. A* **2005**, *109*, 7197–7206.
[13] A. Gossauer, *Die Chemie der Pyrrole*, Springer-Verlag, Berlin, Heidelberg, New York, **1974**, pp. 37–38.
[14] R. A. Jones, G. P. Bean, *The Chemistry of Pyrroles*, Academic Press, London, New York, San Francisco, **1977**, pp. 188–189.
[15] K. P. M. Heirwegh, G. P. Van Hees, P. Leroy, F. P. Van Roy, F. H. Jansen, *Biochem. J.* **1970**, *120*, 877.
[16] T. Yamaguchi, I. Shhiji, A. Sugimoto, Y. Komoda, H. Nakajima, *Biochim. Biophys. Acta* **1996**, *1289*, 110–114.
[17] a) B. A. Trofimov, A. I. Mikhaleva, S. E. Korostova, A. N. Vasil'ev, L. N. Balabanova, *Khim. Geterotsikl. Soedin.* **1977**, 213–214; b) A. I. Mikhaleva, B. A. Trofimov, S. E. Korostova, A. N. Vasil'ev, L. N. Balabanova, *Izv. SO AN SSSR, Ser. Khim. Nauk* **1979**, 107–112; c) B. A. Trofimov, A. I. Mikhaleva, *N-Vinylpirroly*, Nauka, Novosibirsk, **1984**, p. 264 (in Russian); d) B. A. Trofimov in *The Chemistry of Heterocyclic Compounds, Part 2, Vinylpyrroles* (Ed.: R. A. Jones), Wiley, New York, **1992**, vol. 48, pp. 131–298.
[18] a) M. V. Sigalov, E. Yu. Schmidt, A. I. Mikhaleva, S. E. Korostova, I. M. Lasarev, B. A. Trofimov, *Khim. Geterotsykl. Soed.* **1993**, 48–57; b) B. A. Trofimov, M. V. Sigalov, *Main Group Chem. News* **1998**, *6*, 30–41.
[19] a) B. A. Trofimov, "Preparation of Pyrroles from Ketoximes and Acetylenes" in: *Adv. Heterocycl. Chem.* (Ed.:A. R. Katritzky), Acad. Press, San Diego, **1990**, 51, pp. 177–301; b) G. P. Bean, "The Synthesis of 1H-Pyrroles" in: *Pyrroles. Part One. The Synthesis and the Chemical and the Physical Aspects of the Pyrrole Ring* (Ed.: R. A. Jones), Wiley, New York, **1992**, p 105; c) R. J. Tedeschi in *Encyclopedia of Physical Science and Technology*, Acad. Press: San Diego, **1992**, 1, pp. 27–65; d) A. I. Mikhaleva, E. Yu. Schmidt, "Two-step Synthesis of Pyrroles from Ketones and Acetylenes through the Trofimov Reaction" in: *Selected Methods for Synthesis and Modification of Heterocycles* (Ed.: V. G. Kartsev), IBS Press, Moscow, **2002**, 1, pp. 331–352; e) F. Gonzalez, J. F. Sanz-Cervera, R. M. Williams, *Tetrahedron Lett.* **1999**, *40*, 4519–4522.
[20] E. Yu. Schmidt, A. I. Mikhaleva, A. M. Vasil'tsov, A. B. Zaitsev, N. V. Zorina, *Arkivoc* **2005**, *vii, VM-1231J*, 11–17.

[21] M. V. Sigalov, B. A. Trofimov, A. I. Mikhaleva, G. A. Kalabin, *Tetrahedron* **1981**, *37*, 3051–3059.
[22] A. V. Afonin, M. V. Sigalov, V. K. Voronov, E. Yu. Schmidt, B. A. Trofimov, *Izv. AN SSSR, Ser. Khim.* **1987**, 1418–1421.
[23] F. N. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taulor, *J. Chem. Soc., Perkin Trans. 2* **1987**, 1–19.
[24] R. Taylor, O. Kennard, *J. Am. Chem. Soc.* **1982**, *104*, 5063–5070.
[25] T. Steiner, *J. Chem. Soc., Perkin Trans. 2* **1995**, 1315–1319.
[26] G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441–449.
[27] M. Mazik, D. Blaser, R. Boese, *Tetrahedron Lett.* **2000**, *41*, 5827–5831.
[28] A. V. Afonin, M. V. Sigalov, S. E. Korostova, I. A. Aliev, A. V. Vashchenko, B. A. Trofimov, *Magn. Reson. Chem.* **1990**, *28*, 580–586.
[29] Yu. V. Zefirov, P. M. Zorky, *Usp. Khim.* **1995**, *64*, 446–461.
[30] H.-M. Ma, Y.-X. Huang, S.-C. Liang, *Analitica Chim. Acta* **1996**, *334*, 213–219.
[31] D. E. Bergbreiter, P. L. Osburn, C. Li, *Org. Lett.* **2002**, *4*, 737–740.
[32] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347–1363.
[33] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[34] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
[35] R. Krisnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654.
[36] G. M. Sheldrick, *SHELXL 97, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.

Received: April 25, 2006
Published Online: July 10, 2006

