Synthesis, Structure, and Spectral Properties of Bis(pyrrol-2-yl)pyridines

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Keywords: Acetylene / Heterocycles / X-ray absorption spectroscopy / UV/Vis spectroscopy / Fluorescence spectroscopy

2,6-Bis(pyrrol-2-yl)pyridine (**4**), 2-(pyrrol-2-yl)-6-[2-(1-vinylpyrrol-2-yl)]pyridine (**5**), 2,6-bis[2-(1-vinylpyrrol-2-yl)]pyridine (**6**), 2,6-dimethyl-3,5-bis[2-(1-vinylpyrrol-2-yl)] pyridine (**9**), 3-acetyl-2,6-dimethyl-5-[2-(1-vinylpyrrol-2-yl)]pyridine (**10**), and 2,6-dimethyl-3-(pyrrol-2-yl)-5-[2-(1-vinylpyrrol-2-yl)]pyridine (**11**) have been synthesized from the oximes of the corresponding diacetylpyridines in a one-pot procedure by treatment with acetylene in MOH/DMSO systems (M = Li, K) at 80–140 °C under pressures of 25–30 atm, thus illustrating the applicability and general character of the reaction for synthesis of diverse dipyrrole-pyridine assemblies and their *N*-vinyl and acetyl derivatives. A stable **4**·DMSO complex with bifurcated NH···O···HN bonding has been isolated and its X-ray structure determined. Quantum chemical analysis at the B3LYP/6-311G* level shows that the *cis-cis* conformation of **4** is most stable, with the *cis-trans* and *trans-trans* forms accordingly less favorable by 3.2 and 7.8 kcal mol^{-1}. Activation barriers of *cis-cis*-to-*cis-trans* and *cis-trans*-to-*trans-trans* dynamics are 8.3 and 9.5 kcal mol^{-1}, respectively, which means that internal rotation of the pyrrole rings in **4** is essentially hindered.

Introduction

Dipyrroles separated by π-systems are of growing interest for the preparation of conducting materials because their electropolymerization is accompanied by additional stabilization of the intermediate cation radicals, which eliminates such side reactions as β-coupling, cross-linking, and overoxidation resulting in chain defects and degradation of the target polymers.[1] The spacers used in such dipyrroles include ethylenic,[2] cyanoethylenic,[2] diazaethylenic,[3] aldazine,[3] arene,[1,2,4,5] fluorene,[1] naphthalene,[1] carbazole,[1] thiophene,[2] quinoxaline,[6] and tetrazine[7] structures.

At the same time, dipyrroles with pyridine spacers (dipyrrolylpyridines) had until recently been unknown, although they could be useful as monomers for the preparation of alternating poly(dipyrrolylene-pyridinylenes), a new class of prospective conducting polymers that might have unique properties due to their expected high response towards diverse hydrogen bonding partners, metal cations, and pH changes. Like pyridylpyrroles,[8–10] they may display not only high electrical conductivity, but also the capability to form complexes of various chemical natures with better electronic and optoelectronic characteristics than uncomplexed polymers. Luminescent complexes of pyridylpyrroles with boron and zinc compounds have thus been proposed as an alternative to cyclometallated phenylpyridine ligands for use in organic light-emitting diode (OLED) materials,[8] while complexes of pyridylpyrroles with alcohols have been thoroughly explored as model compounds (analogous to pyridylindoles) for investigation of the natures of hydrogen bonds in such biologically important objects as DNA and RNA and for study of the mechanism of photoinduced mutagenesis through intermolecular excited state double proton transfer.[9,10] Polypyridines are known to possess unique combinations of electroactive, coordinative, and optoelectronic properties and offer exceptional prospectives as materials for use in chemical power sources and OLEDs.[11,12] The presence of a pyrrole moiety bound to a bi- or terpyridine ligand significantly improves the Ru complex absorption in the visible region, which is necessary for sunlight harvesting.[13] One may therefore reasonably expect that these properties should be enhanced in poly(dipyrrolylene-pyridinylenes), and that the polymers may acquire new features belonging to neither polypyrroles nor polypyridines alone.

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Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

DOI: 10.1002/ejoc.200500336

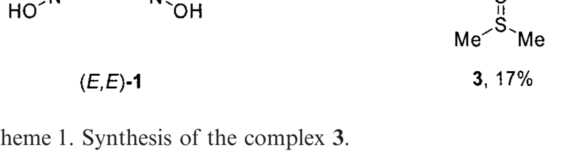
Meanwhile, linking of the pyrrole and pyridine rings still remains a synthetic challenge, and this is even truer if two pyrrole moieties are to be connected with the pyridine nucleus. There are just a few examples of the synthesis of pyridylpyrroles, including the photolysis of pyridylchlorodiazirines in the presence of 1-azabuta-1,3-dienes,[14] heterocyclization of acetylene with oximes of acetylpyridines[15–18] and dimethyl glyoxime[19] (the Trofimov reaction)[20] and the Paal–Knorr high-temperature condensation (170–190 °C) of 1,3-diketones with 2-(aminomethyl)pyridine.[21] Of these methods, none is an obvious candidate to be simply modified for the synthesis of dipyrrolylpyridines. Although the ketoxime-acetylene route may look most appropriate for that, the specificity of oximes of diacetylpyridines, including their enhanced chelating power and that of the intermediates,[22] could seriously interfere with the synthesis.

Here we describe the first successful one-pot syntheses of bis(pyrrol-2-yl)pyridines and their *N*-vinyl derivatives by a significantly modified ketoxime-acetylene methodology. As starting materials, readily accessible dioximes of 2,6-diacetylpyridine (**1**) and 3,5-diacetyl-2,6-dimethylpyridine (**2**) have been employed, covering typical and most readily available parent representatives of the series. We thus illustrate here a prospective general approach to the straightforward synthesis of dipyrroles separated by pyridine spacers based on diacylated pyridines.

Results and Discussion

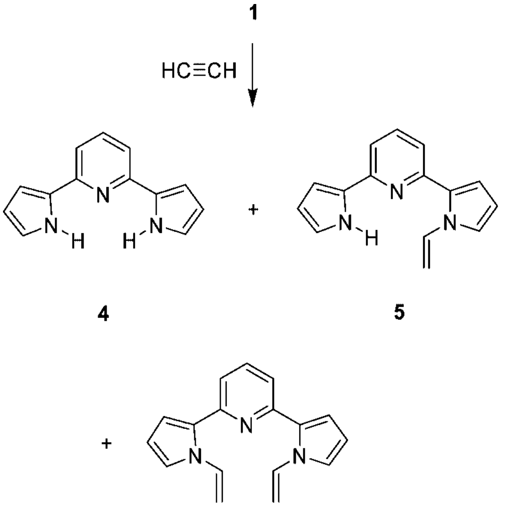
Treatment of 2,6-diacetylpyridine dioximes (**1**) and 3,5-diacetyl-2,6-dimethylpyridine (**2**) with acetylene was carried out under significantly modified conditions [in comparison with those used for the synthesis of pyridylpyrroles[15–18] with LiOH/DMSO (140 °C, 3 h) or KOH/DMSO (120 °C, 1 h) superbase catalytic systems in an autoclave (initial pressure of acetylene at room temperature 10–15 atm, maximum pressure at the reaction temperature 25–30 atm)]. The major modifications included the use of LiOH (instead of KOH) and higher temperatures (140 °C instead of 80–85 °C);[18] in the case of KOH a shorter reactant contact (1 h instead of 3–3.5 h)[15,16,18] and higher dilution were also employed.

In the LiOH/DMSO system, only 2,6-bis(pyrrol-2-yl)pyridine (**4**) is formed from dioxime **1**. The product is first isolated from the reaction mixture as a 1:1 complex with DMSO (**3**; Scheme 1), thus confirming the expected important role of complexation processes in the reaction course.



Scheme 1. Synthesis of the complex **3**.

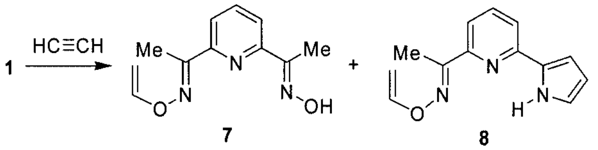
In the KOH/DMSO system, dioxime **1** gave the target dipyrroles **4**–**6** in 25% total yield (Scheme 2).



Scheme 2. Synthesis of dipyrrolylpyridines **4**–**6**.

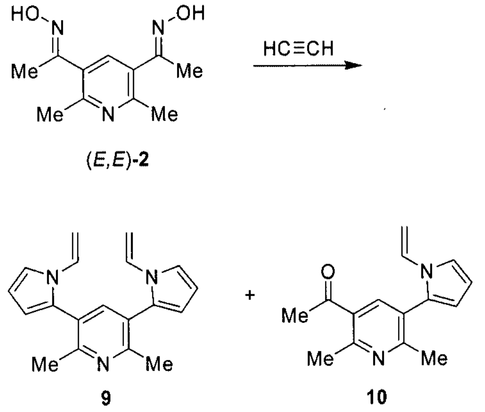
A particular merit of this synthesis is the one-pot simultaneous formation of mono- and divinyl derivatives **5** and **6**, along with nonvinylated dipyrrolylpyridine **4**, all three being easily isolated as individual compounds by column chromatography (Al_2O_3). Obviously, the yields and ratio of the dipyrrolylpyridines **4**–**6** can be controlled by the reaction conditions.

When treatment of dioxime **1** with acetylene is carried out at a lower temperature (80 °C, KOH/DMSO) and for a much shorter time (5 min) the dipyrrole precursors, the *O*-vinyl-2,6-diacetylpyridine dioxime **7** and the 2-(pyrrol-2-yl)-6-[1-(*O*-vinyloxyimino)ethyl]pyridine **8** (*O*-vinyloximes are capable of rearranging to pyrroles[20a,20c,23,24]), are formed (Scheme 3), thus representing a prospective concise synthesis of the first members of the previously unknown classes of functionalized pyridines and pyrroles. Compounds **7** and **8** are readily isolable in pure state by column chromatography (Al_2O_3).



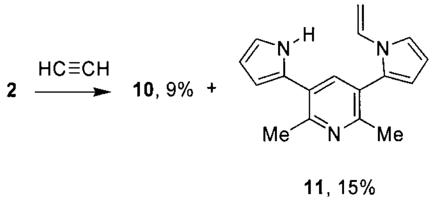
Scheme 3. Synthesis of *O*-vinyloximes **7** and **8**.

In the KOH/DMSO system (120 °C, 1 h), the dioxime **2** reacts with acetylene to afford the target 2,6-dimethyl-3,5-bis[2-(1-vinylpyrrol-2-yl)]pyridine (**9**) and the first representative of another unknown pyridine-pyrrole class – 3-acetyl-2,6-dimethyl-5-[2-(1-vinylpyrrol-2-yl)]pyridine (**10**) – in 12% and 13% isolated yields, respectively (Scheme 4). The formation of **10** was quite unexpected, since ethynylation of the ketone to afford an acetylenic alcohol (the Favorsky reaction) should occur under the reaction conditions, together with autocondensation.



Scheme 4. Synthesis of *N*-vinylpyrroles **9** and **10**.

Treatment of ketoximes with acetylene in the LiOH/DMSO system is known[20a,20c,20e,23] to afford only NH-pyrroles, and no vinylation of these (i.e., formation of *N*-vinylpyrroles) usually takes place. In the case of dioxime **2**, however, the use of the above catalytic system (140 °C, 3 h) unexpectedly yielded vinylpyrroles **10** and **11**, indicating one more peculiarity of the reaction under study in relation to that with the oximes of monoacylated pyridines (Scheme 5).



Scheme 5. Synthesis of *N*-vinylpyrroles **10** and **11**.

The pyrrolization peculiarities of the dioximes **1** and **2** are probably the result of their (*E*,*E*)-configurations, which, as has been demonstrated,[20a,23] are unfavorable for this reaction. The configuration assignment follows from the $^1J_{C(Me)-C=N}$ constant value (43.5 Hz for **1** and 42.1 Hz for **2**), unambiguously indicating the mutual dispositions of substituents at the oxime functions.[25]

The structure of the Pyr$_2$Py·DMSO complex **3** has been confirmed by X-ray analysis (Figures 1 and 2 and Table 1; for additional X-ray data see the Supporting Information). The complex is formed by bifurcated hydrogen bonds between the sulfoxide oxygen and the two NH groups (Figure 1). As a consequence, these are blocked and cannot participate further in the self-assembly of supramolecular structures through intermolecular bond formation with the basic nitrogen atom of the pyridine ring (Figure 2), so ordinary intermolecular contacts are observed in complex **3**.

A structural feature of the complex **3** is the statistical ordering of DMSO molecules (lack of distinction of S1 and S1a atoms) caused by sulfur atom inversion relative to the plane of oxygen and carbon atoms (the "ammonia molecule effect"). Hydrogen bonds between DMSO and pyrrole NH

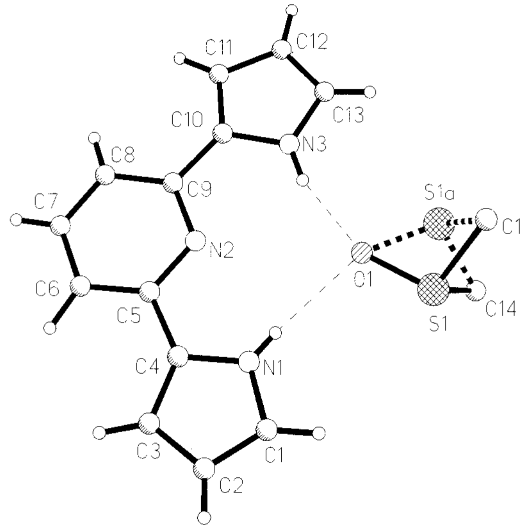


Figure 1. ORTEP diagram of the complex Pyr$_2$Py·DMSO **3** as determined by X-ray diffraction. This compound exists in the solid state as a dual-bonded complex with DMSO.

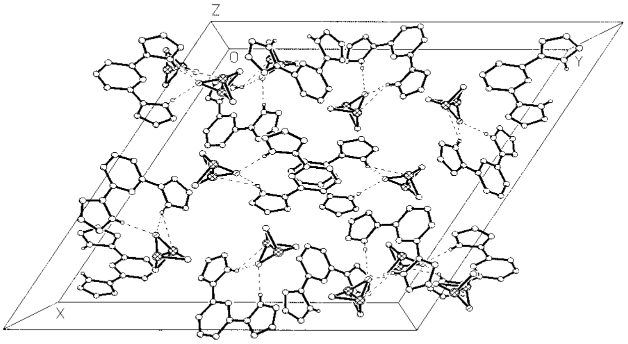


Figure 2. ORTEP diagram of the crystal structure of the complex Pyr$_2$Py·DMSO **3** as determined by X-ray diffraction, shown with all carbon-bound hydrogen atoms omitted.

Table 1. Crystallographic data for the complex **3**.

formula	$C_{15}H_{17}N_3OS$
MW	287.38
crystal system	hexagonal
space group	*R*-3
unit cell dimensions	
a [Å]	*a* = 22.791(3)
b [Å]	*b* = 22.791(3)
c [Å]	*c* = 15.220(3)
V [Å^3]	6846.6(19)
Z	18
D_c [g cm^{-3}]	1.255
μ [mm^{-1}]	0.212
F(000)	2736
ind. reflections	2022
observed reflections	1851
R_{int}	0.0303
GOOF on F^2	0.780
R_1 [$I > 2\sigma(I)$]	0.0299
wR_2 [$I > 2\sigma(I)$]	0.0641

groups in the ten-membered macrocycle formed have the following characteristics:

N(1)–H(1)···O(1): N···H 0.75 Å, H···O 2.22 Å, N···O 2.954 Å, NHO angle 164°;

N(3)–H(3)···O(1): N···H 0.84 Å, H···O 2.11 Å, N···O 2.924 Å, NHO angle 162°.

The tricyclic 2,6-bis(pyrrol-2-yl)pyridine system in the complex **3** is almost planar: the angles between the pyridine ring plane and the planes of pyrrole rings N(1) and N(3) are 0.9 and 2.9°, respectively.

The ^{1}H and ^{13}C NMR parameters of **3** in $CDCl_3$ are close to those of **4**, though shifted slightly upfield in accordance with weak electron transfer from DMSO. As would be expected, the NH signal is shifted by 0.7 ppm to lower field (δNH = 9.62 ppm for **4** and δNH = 10.22 ppm for **3**). Correspondingly, the DMSO signals (δ = 2.59 ppm ^{1}H NMR, 40.9 ppm ^{13}C NMR) are displaced a little towards lower field. The intensity of these signals corresponds to an equimolar ratio of **4** and DMSO, indicating that the complex **3** is strong enough to survive in the $CDCl_3$ solution.

Supporting results for the isolated 2,6-bis(pyrrol-2-yl) pyridine (**4**) were obtained by geometric optimization at the B3LYP/6-311G* level. Three stationary points corresponding to the three conformations – *cis-cis*, *cis-trans*, and *trans-trans* – were located on the potential energy surface. Optimized stationary structures of those three together with their relative energies are shown in Figure 3. It is noteworthy that the energy gap between the most stable *cis-cis* conformation and the *cis-trans* conformation equals ca. 3 kcal mol^{-1} while that between the *cis-cis* conformation and the most unstable *trans-trans* conformation is ca. 8 kcal mol^{-1}. This implies that the population of the predominant *cis-cis* conformation exceeds 99%, which is in keeping with the above X-ray data. The predominance of the *cis-cis* conformation of **4** can be accounted for by the strong intramolecular hydrogen bonding involving pyridine nitrogen and NH protons of both pyrrole moieties (Scheme 6):

Again in line with the X-ray data, all three conformations were found (B3LYP/6-311G*) to be ideally planar, suggesting strong π-electronic conjugation throughout the three aromatic π-systems constituting this remarkable molecule.

As follows from the potential energy curves of the internal rotation of **4** (Figure 4), the barriers of *cis-cis*-to-*cis-trans* and *cis-trans*-to-*trans-trans* transitions are 8.3 and 9.5 kcal mol^{-1}, respectively, meaning that internal rotation of the pyrrole rings around the C(2)–C(2′) bonds is essentially hindered due to the intramolecular hydrogen bonding and the intercyclic π-conjugation.

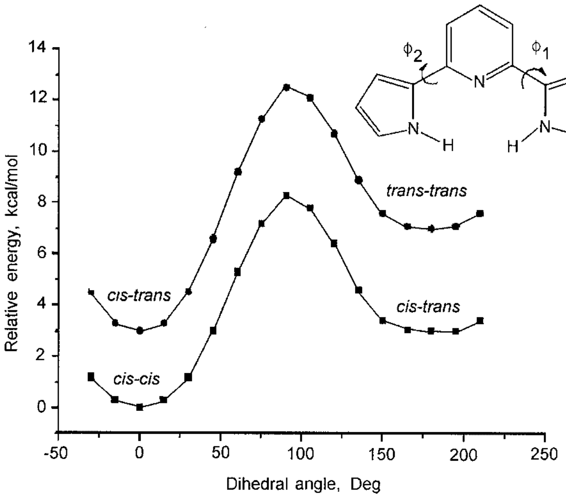
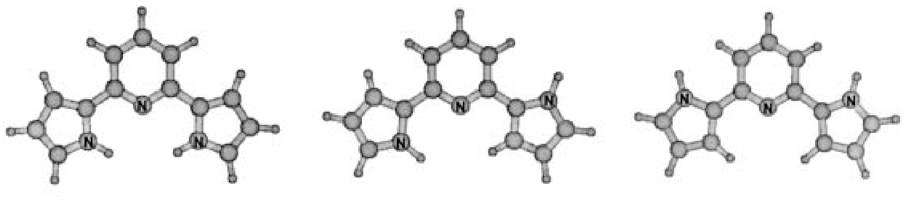


Figure 4. Potential energy curves (B3LYP/6-311G*) for the internal rotation of 2,6-bis(pyrrol-2-yl)pyridine (**4**).

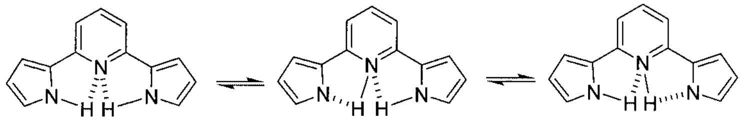
The ease of formation of the peculiar macrocyclic complex **3** with the bifurcational H-bonding between 2,6-bis-(pyrrol-2-yl)pyridine (**4**) and DMSO represents convincing evidence of the large potential of such molecules for non-classical binding of diverse nature.

Preliminary investigation of the optical properties of 2,6-bis(pyrrol-2-yl)pyridine (**4**) and 2,6-bis[2-(1-vinylpyrrol-2-yl)]pyridine (**6**) shows that these molecules have potential for optoelectronics. Thus, exposure of the dipyrrole **4** in powder form to infrared light (1064 nm) results in second



cis-cis (0.0 kcal/mol) *cis-trans* (3.2 kcal/mol) *trans-trans* (7.8 kcal/mol)

Figure 3. Conformations of 2,6-bis(pyrrol-2-yl)pyridine (**4**; relative energies are given in parentheses).



Scheme 6. Intramolecular hydrogen bonding in **4**.

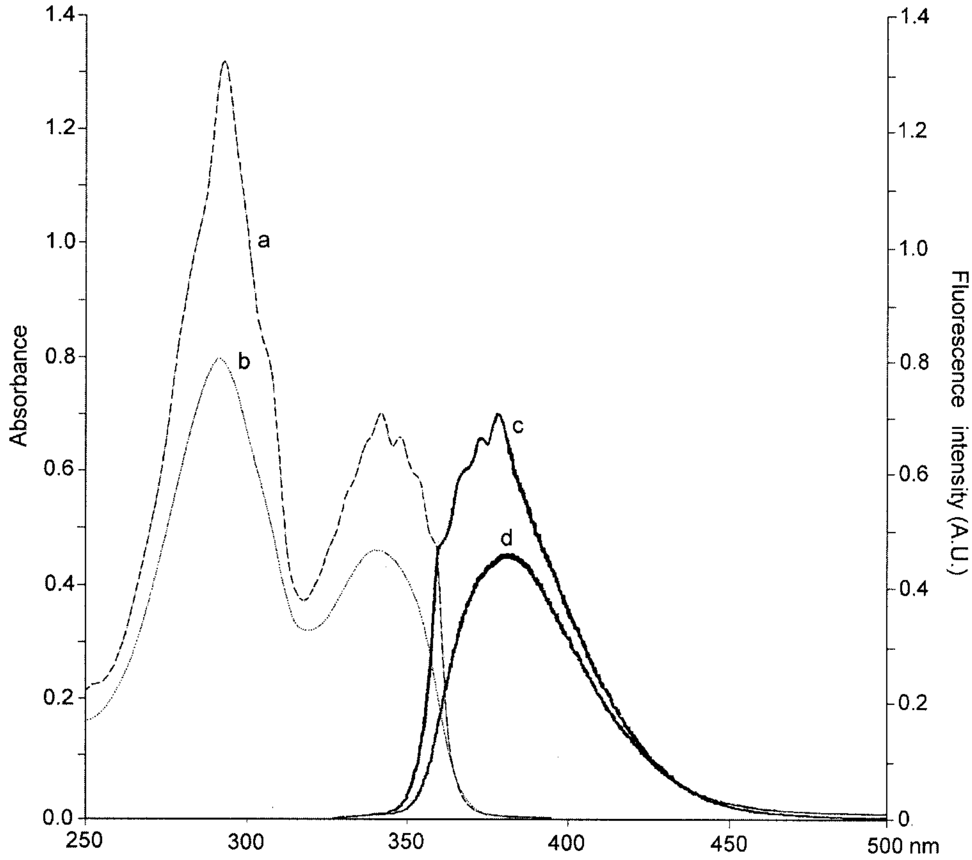


Figure 5. Absorbance (**a**, **b**) and fluorescence (**c**, **d**) spectra of 2,6-bis(pyrrol-2-yl)pyridine (**4**) in *n*-hexane (**a**, **c**) and acetonitrile (**b**, **d**).

harmonic generation (532 nm) with intensity comparable to that of $LiIO_3$, which is known to possess high nonlinearity ($d_{\text{effective}} = 4.1 \times 10^{-12}\,\text{m}\,\text{V}^{-1}$).[26] The divinyl derivative **6**, unlike **4**, does not generate the second harmonic.

Solutions of **4** and **6** show intense fluorescence in the near UV region at room temperature, with quantum yields in hexane of 0.4 and 0.35, respectively. Absorbance and fluorescence spectra of **4** are shown in Figure 5.

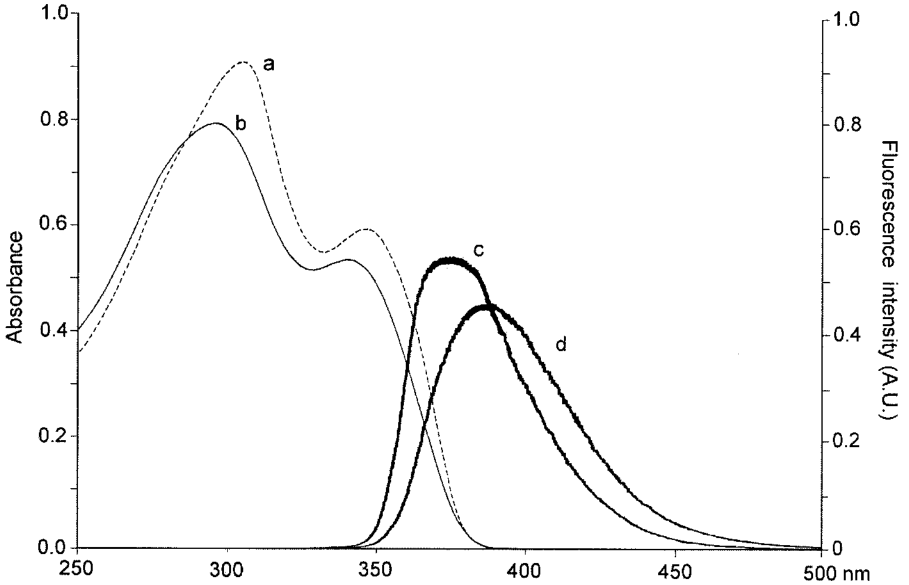


Figure 6. Absorbance (**a**, **b**) and fluorescence (**c**, **d**) spectra of 2,6-bis[2-(1-vinylpyrrol-2-yl)]pyridine (**6**) in *n*-hexane (**a**, **c**) and acetonitrile (**b**, **d**).

The mirror symmetry of long-wavelength absorption band and emission spectrum, as well as the presence of sharply expressed vibrational structure in a nonpolar solvent (*n*-hexane; Figure 5, curves **a** and **c**) indicate a planar structure of **4** in both the ground and the first electron-excited states. Introduction of vinyl groups into **4** (**4** → **6**) results in diffusion of vibrational structure in the absorption and emission spectra but has almost no effect on the efficiency (quantum yield) and wavelength of absorption and fluorescence bands (Figure 6). It may be expected that conducting polymers based on monomers such as **4** and **6** should show fluorescence in the practically important visible part of the spectrum.

Conclusions

A new general approach to the synthesis of previously unknown dipyrroles separated by pyridine spacers is proposed. These compounds show potential for the preparation of new conducting poly(dipyrrolylene-pyridylene) polymers, polyfunctional complexes of various natures, including those with metal cations and H-bonding with organic bases, which may be valuable models for study of steric and electronic effects on associative interactions in DNA and other H-bonded biomolecules, as well as for the design of sensors, photosensitizes for sunlight harvesting, catalysts, and a number of materials for optoelectronics.

Despite the modest yields of the target compounds, the obvious advantages of the methodology, such as one-pot procedures for a number of otherwise inaccessible functionalized pyrrole and pyridine derivatives, inexpensive available starting materials, and cheap catalysts, together with the unexplored potential for optimization and apparent validity for dioximes of diverse substituted diacylpyridines, all make the approach attractive both for larger-scale syntheses and for further improvement and development.

Experimental Section

Instrumental Techniques: ^{1}H and ^{13}C NMR spectra were determined with a Bruker DPX 400 spectrometer at 400.13 and 100.61 MHz, respectively, with HMDS as an internal standard. 2D homonuclear COSY and NOESY routines were used, as well as 2D heteronuclear HSQC and HMBC techniques. IR spectra were recorded on a Bruker IFS 25 spectrometer in KBr pellets. Elemental analysis was performed on a ThermoFinnigan 1112 elemental analyzer. Spectrophotometric and fluorimetric measurements were carried out on a Perkin–Elmer Lambda 35 UV/Vis spectrometer and an experimental luminescence instrument.[27] Second-harmonic generation was carried out in powders by the method proposed by Kurtz and Perri.[28] Harmonic intensity was compared with that of powder prepared from nonlinear $LiIO_3$ crystal. The second harmonic was generated by use of a neodymium-yttrium-aluminium garnet (Nd:YAG) laser with Q-switching at operating wavelength of λ = 1064 nm. Excitation impulse intensity was ca. 10^7 W cm^{-2}. Spectral composition and amplitude of second-harmonic impulse was controlled by use of a photomultiplier and a diffractional monochromator (MDR-23). Chromatographic purification was conducted with standard aluminium oxide 90.

Computational Methods: Geometrical optimizations were performed by use of the GAMESS code,[29] at the DFT-B3LYP level (Becke's three-parameter hybrid functional[30] with nonlocal correlation provided by the Lee, Yang, and Parr correlation functional) [31] with the 6-311G* basis set of Pople and co-workers.[32] No symmetry constraints were applied in any calculations (C_1 symmetry point group was used throughout).

Materials: Commercial grade DMSO (Merck, <0.2% H_2O), LiOH (< 2% H_2O), KOH (≈ 15% H_2O), 2,6-diacetylpyridine (Aldrich), and 3,5-diacetyl-2,6-dimethylpyridine (Aldrich) were used in the experiments. See the Supporting Information for the preparation of dioximes **1** and **2**.

Synthesis of 2,6-Bis(pyrrol-2-yl)pyridine·DMSO Complex 3: A mixture of dioxime **1** (1.00 g, 5.2 mmol), LiOH (0.25 g, 10.4 mmol), and DMSO (25 mL) was placed in a 0.25-L steel rotating autoclave, saturated with acetylene at room temperature (initial pressure 14 atm), and heated at 140 °C for 3 h (maximum pressure was 29 atm, decreasing to 15 atm as the reaction progressed). After cooling, the reaction mixture was discharged from the autoclave, diluted with water to 50 mL volume, and extracted with diethyl ether (5 × 15 mL), and the ether extract was washed with water and dried over K_2CO_3. Removal of ether gave the complex **3** (0.16 g, 17% yield**)**. The structure of **3** was confirmed by X-ray analysis.

2,6-Bis(pyrrol-2-yl)pyridine·DMSO Complex 3 (4·DMSO): Large crystals (prisms), which become reddish in air, m.p. 104–106 °C. ^{1}H NMR ($CDCl_3$): δ = 10.22 (br. s, 2 H, NH), 7.49 (t, $^3J_{3,4}$ = 7.8 Hz, 1 H, 4-H), 7.26 (d, 2 H, 3-H, 5-H), 6.87 (m, 2 H, 5′-H), 6.70 (m, 2 H, 4′-H), 6.27 (m, 2 H, 3′-H), 2.59 [s, 6 H, $(CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 149.7 (C-4), 137.1, 131.8 (C-2, C-3, C-5, C-6), 119.5, 114.9 (C-2′, C-5′), 110.1, 107.2 (C-3′, C-4′), 40.9 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3261, 3218 ($\nu_{NH\cdots O}$), 1593,[a] 1565,[b] 1460 ($\delta_{C\text{–}H}$, CH_3), 1368 ($\delta_{C\text{–}H}$, CH_3), 1294,[a] 1160,[a] 1082,[b] 1056 ($\nu_{O\text{–}S}$), 1017,[b] 740,[b] 647[b] cm^{-1} ([a] for pyridine and [b] for pyrrole moieties); elemental analysis (%) calcd. for $C_{15}H_{17}N_3OS$ (287.38): C 62.69, H 5.96, N 14.62, S 11.16; found: C 62.93, H 6.23, N 14.29, S 10.89.

Synthesis of Pyrroles 4–6: A mixture of dioxime **1** (1.00 g, 5.2 mmol), KOH (0.67 g, 10.35 mmol) and DMSO (20 mL) was placed in a 0.25-L steel rotating autoclave, saturated with acetylene at room temperature (initial pressure 15 atm) and heated at 120 °C for 1 h (maximum pressure was 30 atm, decreased to 15 atm as the reaction progressed). After cooling, the reaction mixture was discharged from the autoclave, diluted with water to 50 mL volume, and extracted with diethyl ether (5 × 15 mL), and the ether extract was washed with water and dried over K_2CO_3. After removal of ether, the residue was subjected to column chromatography (Al_2O_3, eluent: hexane/ether with a gradient of 3:1 to 0:1) to afford of 2,6-bis(pyrrol-2-yl)pyridine (**4**) (0.04 g, 4% yield), 2-(pyrrol-2-yl)-6-[2-(1-vinylpyrrol-2-yl)]pyridine (**5**) (0.07 g, 5% yield), and 2,6-bis[2-(1-vinylpyrrol-2-yl)]pyridine (**6**) (0.19 g,16% yield).

2,6-Bis(pyrrol-2-yl)pyridine (4): White powder, m.p. 185–186 °C. ^{1}H NMR ($CDCl_3$): δ = 9.52 (br. s, 2 H, NH), 7.55 (t, $^3J_{3,4}$ = 7.8 Hz, 1 H, 4-H), 7.27 (d, 2 H, 3-H, 5-H), 6.87 (m, 2 H, 5′-H), 6.69 (m, 2 H, 4′-H), 6.27 (m, 2 H, 3′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 149.7 (C-4), 137.1, 131.8 (C-2, C-3, C-5, C-6), 119.5, 114.9 (C-2′, C-5′), 110.1, 107.2 (C-3′, C-4′) ppm. IR (KBr): $\tilde{\nu}$ = 3427 ($\nu_{N\text{–}H}$), 1590,[a] 1567,[b] 1463,[b] 1294,[a] 1160,[a] 1109,[b] 1087,[b] 1035,[b] 987,[a] 796,[a] 648[b] cm^{-1} ([a] for pyridine and [b] for pyrrole moieties); elemental analysis (%) calcd. for $C_{13}H_{11}N_3$ (209.25): 74.62, H 5.30, N 20.08; found: C, 74.63, H 5.50, N 19.95.

2-(Pyrrol-2-yl)-6-[2-(1-vinylpyrrol-2-yl)]pyridine (5): White powder, m.p. 78–80 °C. ^{1}H NMR ($CDCl_3$): δ = 7.65 (dd, $^3J_{AX}$ = 8.7, $^3J_{BX}$

= 15.7 Hz, 1 H, H_X), 7.60 (t, $^{3}J_{3,4}$ = 7.9 Hz, 1 H, 4-H), 7.35 (d, 1 H, 3-H), 7.23 (d, 1 H, 5-H), 7.17 (m, 1 H, 5′′-H), 6.88 (m, 1 H, 5′-H), 6.70 (m,1 H, 3′-H), 6.56 (m, 1 H, 4′′-H), 6.31 (m, 2 H, 4′-H, 3′′-H), 5.20 (dd, $^{2}J_{AB}$ = 1.2 Hz, 1 H, H_B), 4.76 (dd, 1 H, H_A) ppm. ^{13}C NMR ($CDCl_3$): δ = 150.8 (C-2), 149.5 (C-6), 137.2 (C-4), 134.0 (C_α), 132.6 (C-2′′), 132.0 (C-2′), 120.5 (C-5′′), 119.8 (C-5′), 119.3 (C-3), 115.2 (C-5), 112.0 (C-4′′), 110.4 (C-4′), 110.0 (C-3′′), 107.2 (C-3′), 98.8 (C_β) ppm. IR (KBr): $\tilde{\nu}$ = 3442 ($\nu_{N–H}$), 3136–2875,[a–c] 1639,[c] (ν, C=C), 1590,[a] 1569,[b] 1461,[b] 1417,[c] ($\delta_{C–H}$), 1374,[c] ($\delta_{C–H}$), 1357,[c] 1329 ($\nu_{C–N}$), 1286,[a] 1245,[a] 1158,[a] 1103,[b] 1088,[b] 1072,[b] 1034,[b] 997,[a] 961,[c] 881,[c] 869,[c] 792,[a] 725,[b] 672,[b] 647,[b] 591[b] cm^{-1} ([a] for pyridine, [b] for pyrrole, and [c] for vinyl moieties); elemental analysis (%) calcd. for $C_{15}H_{13}N_3$ (235.29): C 76.57, H 5.57, N 17.86; found: C 76.69, H 5.66, N 17.63.

2,6-Bis[2-(1-vinylpyrrol-2-yl)]pyridine (6): White crystals, m.p. 94–96 °C. ^{1}H NMR ($CDCl_3$): δ = 7.95 (dd, $^{3}J_{BX}$ = 15.7, $^{3}J_{AX}$ = 8.7 Hz, 2 H, H_X), 7.63 (t, $^{3}J_{3,4}$ = 8.2 Hz, 1 H, 4-H), 7.35 (d, 2 H, 3-H, 5-H), 7.19 (dd, $^{3}J_{4′,5′}$ = 2.7, $^{4}J_{3′,5′}$ = 1.7 Hz, 2 H, 5′-H), 6.62 (dd, 2 H, 3′-H), 6.28 (dd, 2 H, 4′-H), 5.16 (dd, $^{2}J_{AB}$ = 1.2 Hz, 2 H, H_B), 4.70 (dd, 2 H, H_A) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.0 (C-2, C-6), 137.1 (C_α), 134.3 (C-4), 132.3 (C-2′), 120.7, 119.3 (C-3, C-5, C-5′), 112.5, 110.0 (C-3′, C-4′), 99.2 (C_β) ppm. IR (KBr): $\tilde{\nu}$ = 3139–2861,[a–c] 1641,[c] ($\nu_{C=C}$), 1569,[a] 1472,[b] 1453,[b] 1427,[c] 1378,[c] 1355,[c] 1333 (ν, $_{C–N}$), 1283,[a] 1250,[a] 1200, 1157,[a] 1097,[b] 1071,[b] 990,[a] 977,[c] 961,[c] 873,[c] 820,[a] 795,[a] 771,[a] 726,[b] 713,[b] 664,[b] 649,[b] 591[c] cm^{-1} ([a] for pyridine, [b] for pyrrole, and [c] for vinyl moieties); elemental analysis (%) calcd. for $C_{17}H_{15}N_3$ (261.35): C 78.13, H 5.79, N 16.08; found: C 78.01, H 5.75, N 15.92.

Synthesis of *O*-Vinyloximes 7 and 8: A mixture of dioxime **1** (1.00 g, 5.2 mmol) and KOH (0.67 g, 10.35 mmol) in DMSO (20 mL) was placed in a 0.25-L steel rotating autoclave, saturated with acetylene at room temperature (initial pressure 15 atm), and then heated at 80 °C for 5 min (maximum pressure was 21 atm, reduced to 16 atm as the reaction progressed). After cooling, the reaction mixture was discharged, diluted with water to 50 mL volume, and extracted with diethyl ether (5 × 15 mL), and the ether extract was washed with water and dried over K_2CO_3. After removal of ether, the residue was subjected to column chromatography (Al_2O_3, eluent: hexane/ether, 3:1, no gradient was employed; R_f(**7**) = 0.63, R_f(**8**) = 0.41) to afford *O*-vinyl-2,6-diacetylpyridine dioxime **7** (0.03 g, 3% yield) and 2-(pyrrol-2-yl)-6-[1-(*O*-vinyloxyimino)ethyl]pyridine (**8**, 0.06 g, 8%).

***O*-Vinyl-2,6-diacetylpyridine Dioxime {2-[1-(Hydroxyiminylimino) ethyl]-6-[1-(*O*-vinyloxyimino)ethyl]pyridine} (7):** White powder, m.p. 116–118 °C, ^{1}H NMR ($CDCl_3$): δ = 7.85, 7.83 (d, $^{3}J_{3,4}$ = 7.8 Hz, 2 H, 3-H, 5-H), 7.67 (t, 1 H, 4-H), 7.05 (dd, $^{3}J_{BX}$ = 14.2, $^{3}J_{AX}$ = 6.9 Hz, 1 H, H_X), 4.72 (dd, $^{2}J_{AB}$ = 1.2 Hz, 1 H, H_B), 4.21 (dd, 2 H, H_A), 2.44, 2.39 [s, 6 H, $(CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$): δ = 158.4, 157.4 (C=N), 153.8, 153.3, 152.5 (C-2, C-6, C_α), 136.6 (C-4), 120.7, 120.6 (C-3, C-5), 88.7 (C_β), 11.7, 10.3 $(CH_3)_2$ ppm. IR (KBr): $\tilde{\nu}$ = 3316, 3263 ($\nu_{O–H}$), 3117–2859 (br., $\nu_{C–H}$), 1646 ($\nu_{C=C}$) cm^{-1}; elemental analysis (%) calcd. for $C_{11}H_{13}N_3O_2$ (219.24): C 60.26, H 5.98, N 19.17; found: C 60.56, H 6.34, N 18.99.

2-(Pyrrol-2-yl)-6-[1-(*O*-vinyloxyimino)ethyl]pyridine (8): White powder, m.p. 86–88 °C. ^{1}H NMR ($CDCl_3$): δ = 9.51 (br. s, 1 H, NH), 7.65 (d, $^{3}J_{3,4}$ = 7.8 Hz, 1 H, 5-H), 7.61 (t, 1 H, 4-H), 7.50 (d, 1 H, 3-H), 7.05 (dd, $^{3}J_{BX}$ = 14.2, $^{3}J_{AX}$ = 6.9 Hz, 1 H, H_X), 6.92 (m, 1 H, 5′-H), 6.71 (m, 1 H, 3′-H), 6.29 (m, 1 H, 4′-H), 4.72 (dd, $^{2}J_{AB}$ = 1.2 Hz, 1 H, H_B), 4.21 (dd, 2 H, H_A) ppm. ^{13}C NMR ($CHCl_3$): δ = 158.4 (C=N), 152.9 (C_α), 152.6 (C-2), 149.8 (C-6), 136.9 (C-4), 131.4 (C-2′), 119.9 (C-5′), 118.4 (C-5), 117.7 (C-3), 110.5 (C-4′), 107.4 (C-3′), 88.7 (C_β), 12.0 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3412 ($\nu_{N–H}$), 3117–2859,[a–c] ($\nu_{C–H}$), 1641,[c] ($\nu_{C=C}$), 1610,[a] 1585,[a] 1566,[a] 1460,[b] 1412,[c] 1367,[c] 1336 ($\nu_{C–N}$), 1285,[a] 1162,[a] 1113,[b] 1099,[b] 1087,[b] 1062,[b] 1038,[b] 1012,[b] 976,[c] 881,[c] 800,[a] 733,[b] 695,[c] 653,[b] 640,[b] 595,[c] 580[c] cm^{-1} ([a] for pyridine, [b] for pyrrole, and [c] for vinyl moieties); elemental analysis (%) calcd. for $C_{13}H_{13}N_3O$ (227.27): C 68.71, H 5.77, N 18.49; found: C 68.39, H 5.63, N 18.54.

Synthesis of 2,6-Dimethyl-3,5-bis[2-(1-vinylpyrrol-2-yl)]pyridine (9) and 3-Acetyl-2,6-dimethyl-5-[2-(1-vinylpyrrol-2-yl)]pyridine (10): A mixture of dioxime **2** (0.50 g, 2.3 mmol) and KOH (0.26 g, 4.6 mmol) in DMSO (20 mL) was placed in a 0.25-L steel rotating autoclave, saturated with acetylene at room temperature (initial pressure 11 atm) and heated at 120 °C for 1 h (maximum pressure was 22 atm, reduced to 10 atm as the reaction progressed). After cooling, the reaction mixture was discharged, diluted with water to 50 mL volume, and extracted with diethyl ether (5 × 15 mL), and the ether extract was washed with water and dried over K_2CO_3. After removal of ether, the residue was subjected to column chromatography (Al_2O_3, eluent: hexane/ether with a gradient of 3:1 to 0:1) to afford 3,5-bis[2-(1-vinylpyrrol-2-yl)]-2,6-dimethylpyridine (**9**, 0.08 g, 12% yield) and 3-acetyl-2,6-dimethyl-5-[2-(1-vinylpyrrol-2-yl)]pyridine (**10**, 0.07 g 13% yield) .

2,6-Dimethyl-3,5-bis[2-(1-vinylpyrrol-2-yl)]pyridine (9): White crystals, m.p. 87–90 °C. ^{1}H NMR ($CDCl_3$): δ = 7.38 (s, 1 H, 4-H), 7.11 (m, 2 H, 5′-H), 6.52 (dd, $^{3}J_{BX}$ = 15.7, $^{3}J_{AX}$ = 8.7 Hz, 2 H, H_X), 6.29 (m, 2 H, 4′-H), 6.14 (m, 2 H, 3′-H), 5.08 (dd, $^{2}J_{AB}$ = 1.2 Hz, 2 H, H_B), 4.59 (dd, 2 H, H_A) ppm. ^{13}C NMR ($CDCl_3$): δ = 157.7 (C-2, C-6), 141.7 (C-4), 131.0 (C_α), 130.4 (C-2′), 124.7 (C-3, C-5), 117.3 (C-5′), 111.1 (C-3′), 110.2 (C-4′), 98.4 (C_β), 23.1 [2,6-$(CH_3)_2$] ppm. IR (KBr): $\tilde{\nu}$ = 3140–2863 ($\nu_{C–H}$), 1642,[a] ($\nu_{C=C}$), 1545,[b] 1479 ($\delta_{C–H}$, CH_3), 1453,[b] 1429,[b] 1349 ($\delta_{C–H}$, CH_3), 1287,[c] 1256,[c] 1176,[b] 1073,[b] 1027,[b] 966,[a] 929, 820,[c] 796,[c] 716,[b] 591[a] cm^{-1} ([a] for vinyl, [b] for pyrrole, and [c] for pyridine moieties); elemental analysis (%) calcd. for $C_{19}H_{19}N_3$ (289.38): C 78.86, H 6.62, N 14.52; found: C 78.51, H 6.49, N 14.63.

3-Acetyl-2,6-dimethyl-5-[2-(1-vinylpyrrol-2-yl)]pyridine (10): White crystals, m.p. 82–84 °C, ^{1}H NMR ($CDCl_3$): δ = 7.82 (s, 1 H, 4-H), 7.14 (m, 1 H, 5′-H), 6.45 (dd, $^{3}J_{BX}$ = 15.7, $^{3}J_{AX}$ = 8.7 Hz, 1 H, H_X), 6.33 (m, 1 H, 4′-H), 6.18 (m, 1 H, 3′-H), 5.11 (dd, $^{2}J_{AB}$ = 1.2 Hz, 1 H, H_B), 4.62 (dd, 1 H, H_A), 2.77 (s, 3 H, COCH_3), 2.55 (s, 3 H, 2-CH_3), 2.40 (s, 3 H, 6-CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 199.8 (C=O), 161.0 (C-6), 157.9 (C-2), 140.1 (C-4), 130.8 (C_α), 129.8 (C-3, C-2′), 124.8 (C-5), 117.7 (C-5′), 111.2 (C-3′), 110.3 (C-4′), 98.9 (C_β), 29.3 (COCH_3), 24.8 (2-CH_3), 23.4 (6-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3140–2863 ($\nu_{C–H}$), 1642,[a] ($\nu_{C=C}$), 1545,[b] 1479 ($\delta_{C–H}$, CH_3), 1453,[b] 1429,[b] 1349 ($\delta_{C–H}$, CH_3), 1287,[c] 1256,[c] 1176,[b] 1146, 1073,[b] 1027,[b] 966,[a] 820,[c] 796,[c] 716,[b] 591[a] cm^{-1} ([a] for vinyl, [b] for pyrrole, and [c] for pyridine moieties); elemental analysis (%) calcd. for $C_{15}H_{16}N_2O$ (240.30): C 74.97, H 6.71, N 11.66; found: C 74.67, H 6.78, N 11.63.

Synthesis of 2,6-Dimethyl-3-(pyrrol-2-yl)-5-[2-(1-vinylpyrrol-2-yl)]-pyridine (11): A mixture of dioxime **4** (0.50 g, 2.3 mmol) and KOH (0.26 g, 4.6 mmol) in DMSO (20 mL) was placed in a 0.25-L steel rotating autoclave, saturated with acetylene at room temperature (initial pressure 12 atm), and heated at 140 °C for 3 h (maximum pressure was 30 atm, reduced to 19 atm as the reaction progressed). After cooling, the reaction mixture was discharged, diluted with water to 50 mL volume, and extracted with diethyl ether (5 × 15 mL), and the ether extract was washed with water and dried over K_2CO_3. After removal of ether, the residue was subjected to column chromatography (Al_2O_3, eluent: hexane/ether with a gradient of 1:0 to 0:1) to afford 2,6-dimethyl-3-(pyrrol-2-yl)-5-[2-(1-vinylpyrrol-2-yl)]pyridine (**11**, 0.09 g, 15% yield) and 3-acetyl-2,6-dimethyl-5-[2-(1-vinylpyrrol-2-yl)]pyridine (**10**, 0.05 g, 9% yield).

2,6-Dimethyl-3-(pyrrol-2-yl)-5-[2-(1-vinylpyrrol-2-yl)]pyridine (11): White crystals, m.p. 85–88 °C. ^{1}H NMR (CDCl$_3$): δ = 8.43 (br.s, 1 H, NH), 7.49 (m, 1 H, 4-H), 7.12 (m, 1 H, 5′′-H), 6.88 (m, 1 H, 5′-H), 6.50 (dd, $^3J_{BX}$ = 15.7, $^3J_{AX}$ = 8.7 Hz, 1 H, H$_X$), 6.39 (m, 1 H, 3′-H), 6.32 (m, 2 H, 4′-H, 4′′-H), 6.13 (m, 1 H, 3′′-H), 5.05 (dd, $^2J_{AB}$ = 1.2 Hz, 1 H, H$_B$), 4.58 (dd, 1 H, H$_A$), 2.70 (s, 3 H, 6-CH_3), 2.37 (s, 3 H, 2-CH_3) ppm. ^{13}C NMR (CDCl$_3$): δ = 155,7 (C-2), 154.3 (C-6), 138.0 (C-4), 131.0 (C$_\alpha$), 130.7 (C-2′′), 128.8 (C-2′), 125.5 (C-5), 125.1 (C-3), 119.0 (C-5′), 117.2 (C-5′′), 110.8 (C-3′′), 110.2 (C-4′′), 109.8 (C-4′), 109.5 (C-3′), 98.3 (C$_\beta$), 24.1 (6-CH_3), 22.8 (2-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3378 (ν_{N-H}), 3104–2857 (ν_{C-H}), 1642,[a] ($\nu_{C=C}$), 1602,[b] 1555,[c] 1538,[c] 1478 (δ_{C-H}, CH_3), 1375 (δ_{C-H}, CH_3), 1350 (δ_{C-H}, CH_3), 1306 (ν_{C-N}), 1291,[b] 1286,[b] 1255,[b] 1162,[c] 1126,[c] 1109,[c] 1076,[c] 1029,[c] 965,[a] 799,[b] 720,[c] 593[a] cm^{-1} ([a] for vinyl, [b] for pyridine, and [c] for pyrrole moieties); elemental analysis (%) calcd. for C$_{17}$H$_{17}$N$_3$ (263.34): C 77.54, H 6.51, N 15.96; found: C 77.29, H 6.58, N 15.63.

CCDC-267654 for complex **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.

Supporting Information: The Supporting Information (see footnote on the first page of this article) contains description of the synthesis of dioximes **1** and **2** and additional X-ray data for **3**, as well as bond lengths and angles, atomic coordinates and anisotropic displacement parameters.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (grants No. 03-03-32472 and No. 2241.2003.3) and the Presidium of the Russian Academy of Sciences (grant No. 10002-251/P-25/155-305/200404-072).

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Received: May 11, 2005
Published Online: September 1, 2005