

Dedicated to Full Member of the Russian Academy of Sciences  
N.S. Zefirov on His 70th Anniversary

# $^1\text{H}$ and $^{13}\text{C}$ NMR Study of Bifurcated Intramolecular Hydrogen Bonds in 2,6-Bis(2-pyrrolyl)pyridine and 2,6-Bis(1-vinyl-2-pyrrolyl)pyridine

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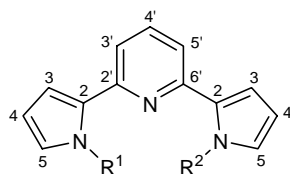
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**Abstract**—According to the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data, bifurcated intramolecular hydrogen bond  $\text{NH}\cdots\text{N}\cdots\text{HN}$  in 2,6-bis(2-pyrrolyl)pyridine fixes its molecule in a conformation with *syn* orientation of the pyrrole rings. An analogous bifurcated hydrogen bond  $\text{CH}\cdots\text{N}\cdots\text{HC}$  is formed in 2,6-bis(1-vinyl-2-pyrrolyl)pyridine. 2-(1-Vinyl-2-pyrrolyl)-6-(2-pyrrolyl)pyridine is characterized by unsymmetrical bifurcated hydrogen bond  $\text{NH}\cdots\text{N}\cdots\text{HC}$ .

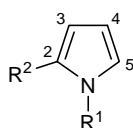
Systematic studies on the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a wide series of pyrrole derivatives [1–7] allowed us to distinguish 2-hetarylpyrroles as a class of compounds giving rise to various intramolecular hydrogen bonds. For example, a weak intramolecular hydrogen bond  $\text{CH}\cdots\text{N}$  between the  $\alpha$ -hydrogen atom of the vinyl group and pyridine nitrogen atom was found in 1-vinyl-2-(2-pyridyl)pyrrole [6]. 2-(2-Pyridyl)pyrrole is characterized by a weak intramolecular hydrogen bond  $\text{NH}\cdots\text{N}$  between the pyrrole N–H atom and pyridine nitrogen atom [4]. The  $^1\text{H}$  NMR and IR spectra of 5-(2-pyridyl)-2-trifluoroacetylpyrrole revealed a bifurcated hydrogen bond involving both pyridine nitrogen atom and carbonyl oxygen atom of the trifluoroacetyl group [4, 5]. In continuation of our studies on intra-

molecular hydrogen bonds in pyrrole derivatives, in the present work we examined the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2,6-bis(2-pyrrolyl)pyridine (**I**) and 2,6-bis(1-vinyl-2-pyrrolyl)pyridine (**VI**) and compared the results with those found for model compounds **II–V** and **VII–XIV**.

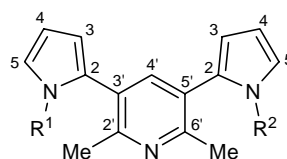
The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of pyrroles **I–XIV** are given in Tables 1 and 2, and the  $^{13}\text{C}$ – $^1\text{H}$  coupling constants are collected in Table 3. Following the previously used algorithm for studying 2-hetarylpyrroles by NMR spectroscopy, let us consider first the character of  $\pi,\pi$  conjugation between the heterorings in compounds **I** and **VI** on the basis of the corresponding carbon chemical shifts. We showed in [4] that the signals from  $\text{C}^{3'}$  and  $\text{C}^{5'}$  in the pyridine ring of



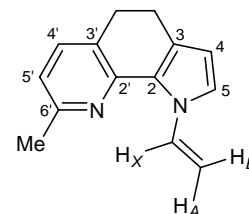
**I, VI, XII**



**II–V, VIII–XI**



**VII, XIII**



**XIV**

**I–V**,  $\text{R}^1 = \text{H}$ ; **I**,  $\text{R}^2 = \text{H}$ ; **II**,  $\text{R}^2 = 2\text{-pyridyl}$ ; **III**,  $\text{R}^2 = 3\text{-pyridyl}$ ; **IV**,  $\text{R}^2 = 4\text{-pyridyl}$ ; **V**,  $\text{R}^2 = \text{Ph}$ ; **VI–XIII**,  $\text{R}^1 = \text{CH}_2=\text{CH}$ ;  
**VI, VII**,  $\text{R}^2 = \text{CH}_2=\text{CH}$ ; **VIII**,  $\text{R}^2 = 2\text{-pyridyl}$ ; **IX**,  $\text{R}^2 = 3\text{-pyridyl}$ ; **X**,  $\text{R}^2 = 4\text{-pyridyl}$ ; **XI**,  $\text{R}^2 = \text{Ph}$ ; **XII, XIII**,  $\text{R}^2 = \text{H}$ .

**Table 1.** <sup>13</sup>C NMR spectra of compounds **I–XIV**

Comp. no.	Chemical shifts $\delta_C$ , ppm										
	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>	C <sup>2'</sup>	C <sup>3'</sup>	C <sup>4'</sup>	C <sup>5'</sup>	C <sup>6'</sup>	C <sup><math>\alpha</math></sup>	C <sup><math>\beta</math></sup>
<b>I</b>	131.77	107.19	110.14	119.53	149.73	114.87	137.07	114.87	149.73	–	–
<b>II</b>	131.64	107.27	110.29	119.99	150.76	118.24	136.56	120.52	148.91	–	–
<b>III</b>	129.29	107.28	110.26	120.35	144.99	128.64	131.28	123.86	146.48	–	–
<b>IV</b>	129.31	109.11	110.95	121.21	150.23	117.84	139.68	117.84	150.23	–	–
<b>V</b>	132.13	106.02	110.20	118.89	132.78	123.92	128.96	126.97	–	–	–
<b>VI</b>	132.23	112.50	110.02	120.61	150.97	119.30	137.09	119.30	150.97	134.22	99.17
<b>VII<sup>a</sup></b>	130.43	111.08	110.21	117.35	157.70	124.68	141.70	124.68	157.70	131.03	98.39
<b>VIII</b>	131.40	111.78	109.56	119.66	151.27	121.59	135.78	120.10	148.04	133.04	98.00
<b>IX</b>	130.33	111.13	110.31	119.49	149.60	128.41	136.10	123.14	148.02	131.35	100.19
<b>X</b>	130.88	112.09	110.37	121.05	149.49	122.55	139.70	122.55	149.49	131.56	101.02
<b>XI</b>	134.39	110.15	110.12	118.35	132.52	128.49	129.39	127.28	–	132.08	98.81
<b>XII</b>	132.60	110.04	112.03	120.54	150.81	119.32	137.22	115.24	149.49	133.98	98.83
	131.78	107.19	110.43	119.84							
<b>XIII<sup>a</sup></b>	130.70	110.82	110.20	117.20	155.65	125.08	138.01	125.55	154.31	131.00	98.28
	128.78	109.53	109.78	118.99							
<b>XIV<sup>b</sup></b>	127.11	126.45	108.79	118.95	149.00	127.89	135.32	118.88	154.86	134.23	96.81

<sup>a</sup> Chemical shifts of the CH<sub>3</sub> carbon atom,  $\delta_C$ , ppm: **VII**, 23.12; **XIII**, 22.81, 24.07.<sup>b</sup>  $\delta_C$ , ppm: 24.30 (CH<sub>3</sub>); 22.00, 29.31 (CH<sub>2</sub>CH<sub>2</sub>).**Table 2.** <sup>1</sup>H NMR and IR spectra of compounds **I–XIV**

Comp. no.	Chemical shifts $\delta$ , ppm												IR spectrum, $\nu(\text{NH})$ , cm <sup>-1</sup>
	3-H	4-H	5-H	2'-H	3'-H	4'-H	5'-H	6'-H	H <sub>A</sub>	H <sub>B</sub>	H <sub>X</sub>	NH	
<b>I</b>	6.76	6.31	6.92	–	7.38	7.66	7.38	–	–	–	–	9.52	3468
<b>II</b>	6.69	6.27	6.87	–	7.52	7.59	7.00	8.43	–	–	–	9.62	3460
<b>III</b>	6.57	6.34	6.90	8.72	–	7.76	7.24	8.38	–	–	–	8.63	3478
<b>IV</b>	6.73	6.32	6.94	8.51	7.33	–	7.33	8.51	–	–	–	8.75	3482
<b>V</b>	6.51	6.28	6.84	7.45	7.34	7.18	7.34	7.45	–	–	–	8.43	3484
<b>VI</b>	6.62	6.27	7.18	–	7.35	7.62	7.35	–	4.69	5.16	7.96	–	
<b>VII<sup>a</sup></b>	6.15	6.30	7.12	–	–	7.39	–	–	4.60	5.09	6.52	–	
<b>VIII</b>	6.57	6.27	7.18	–	7.45	7.60	7.05	8.58	4.72	5.16	7.90	–	
<b>IX</b>	6.31	6.31	7.14	8.64	–	7.66	7.31	8.53	4.76	5.20	6.82	–	
<b>X</b>	6.38	6.25	7.09	8.52	7.23	–	7.23	8.52	4.77	5.19	6.85	–	
<b>XI</b>	6.23	6.26	7.07	7.34	7.32	7.27	7.32	7.34	4.53	5.12	6.86	–	
<b>XII</b>	6.33	6.60	7.22	–	7.29	7.64	7.40	–	4.79	5.24	7.68	9.52	3450
	6.75	6.33	6.94										
<b>XIII</b>	6.31	6.40	7.13	–	–	7.49	–	–	4.58	5.08	6.50	8.43	3475
	6.13	6.31	6.88										
<b>XIV<sup>b</sup></b>	–	6.09	7.12	–	–	7.28	6.75	–	4.67	5.10	8.61	–	

<sup>a</sup>  $\delta(\text{CH}_3)$  2.41 ppm.<sup>b</sup>  $\delta$ , ppm: 2.47 (CH<sub>3</sub>); 2.69, 2.82 (CH<sub>2</sub>CH<sub>2</sub>).

**Table 3.** Direct  $^{13}\text{C}$ - $^1\text{H}$  coupling constants ( $^1J_{\text{CH}}$ , Hz) in the  $^{13}\text{C}$  NMR spectra of compounds **I–XII** and **XIV**

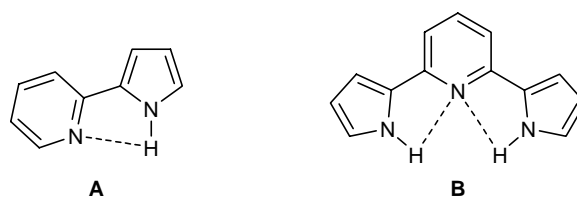
Comp. no.	C <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>	C <sup>2'</sup>	C <sup>3'</sup>	C <sup>4'</sup>	C <sup>5'</sup>	C <sup>6'</sup>	C <sup>β</sup> -H <sub>A</sub>	C <sup>β</sup> -H <sub>B</sub>	C <sup>α</sup> -H <sub>X</sub>
<b>I</b>	170.5	171.0	183.8	–	164.1	162.7	164.1	–	–	–	–
<b>II</b>	168.9	177.7	184	–	162.8	162.6	164.0	177.4	–	–	–
<b>III</b>	169.6	171.9	184.8	179.7	–	160.9	163.0	176.8	–	–	–
<b>IV</b>	170.6	172.0	186.4	177.4	161.9	–	161.9	177.4	–	–	–
<b>V</b>	169.7	171.3	185.5	157.3	160.0	161.8	160.0	157.3	–	–	–
<b>VI</b>	169.5	171.4	185.9	–	164.9	164.5	164.9	–	163.0	156.4	181.3
<b>VII</b>	171.4	171.9	185.7	–	–	162.2	–	–	163.6	157.1	175.1
<b>VIII</b>	171.3	172.8	185.9	–	164.1	162.3	163.6	178.0	163.3	156.6	180.7
<b>IX</b>	171.2	172.4	186.1	179.6	–	163.2	162.1	179.9	163.8	157.4	176.5
<b>X</b>	171.5	173.1	187.2	178.6	163.2	–	163.2	178.6	163.9	157.7	176.7
<b>XI</b>	171.1	171.7	185.7	160.1	160.5	161.3	160.5	160.1	163.5	157.0	176.1
<b>XII</b>	172.8 169.1	171.0 171.4	185.2 185.7	–	164.1	163.6	162.7	–	163.2	156.8	180.2
<b>XIV</b>	–	170.6	185.0	–	–	157.7	160.9	–	163.2	155.8	181.7

2-(2-pyridyl)pyrrole (**II**) are displaced upfield by 4 and 6 ppm, respectively, due to  $\pi,\pi$  conjugation between the pyridine and pyrrole rings. 2,6-Bis(2-pyrrolyl)pyridine (**I**) shows in the  $^{13}\text{C}$  NMR spectrum analogous shifts of the C<sup>3'</sup> and C<sup>5'</sup> signals relative to those typical of 2-(2-pyridyl)pyrrole (**II**) as a result of  $\pi,\pi$  conjugation with the second pyrrole ring. The chemical shifts of the pyrrole carbon nuclei in molecules **I** and **II** are almost identical. These data suggest that the strength of  $\pi,\pi$  conjugation between each of the pyrrole rings and the pyridine ring in **I** is the same as the strength of  $\pi,\pi$  conjugation between the only pyrrole ring and the pyridine ring in 2-(2-pyridyl)pyrrole (**II**) and that there is no mutual effect of the pyrrole rings in 2,6-bis(2-pyrrolyl)pyridine (**I**).

Analogous comparison of the chemical shifts in the  $^{13}\text{C}$  NMR spectra of 2,6-bis(1-vinyl-2-pyrrolyl)pyridine (**VI**) and 1-vinyl-2-(2-pyridyl)pyrrole (**VIII**) leads to somewhat different conclusions. In this case, the shifts of the C<sup>3'</sup> and C<sup>5'</sup> signals due to conjugation with the second pyrrole ring are considerably smaller ( $\Delta\delta_{\text{C}} = 1\text{--}2$  ppm, Table 1). However, the chemical shifts of the pyrrole carbon atoms in **VI** and **VIII** differ appreciably. Particular attention should be given to the downfield shift of the signal from the  $\beta$ -carbon atom in the vinyl group of **VI** ( $\Delta\delta_{\text{C}} = 1.2$  ppm relative to **VIII**, Table 1). Thus we clearly observe mutual influence of the pyrrole rings in molecule **VI**. On the other hand, such effect is absent in molecule **I**. In order to ration-

alize these findings, a more detailed examination of the steric structure of the above compounds and intramolecular interactions occurring therein should be performed.

2-(2-Pyridyl)pyrrole (**II**) exists as a conformer with *syn* arrangement of the heteroring, which is stabilized by intramolecular hydrogen bond NH $\cdots$ N (structure **A**) [4]. The formation of that bond follows from the sharp downfield shift of the NH proton signal in the  $^1\text{H}$  NMR spectrum of 2-(2-pyridyl)pyrrole (**II**), as compared to structurally related compounds **III–V** ( $\Delta\delta = 0.9\text{--}1.2$  ppm, Table 2). The *syn* orientation of the heterorings in molecule **II** is confirmed by the lack of an appreciable downfield shift of the pyrrole 3-H signal; in addition, the coupling constant  $^1J_{\text{C-3-H}}$  does not increase [4]. The chemical shifts of the NH and 3-H protons in the  $^1\text{H}$  NMR spectrum of 2,6-bis(2-pyrrolyl)pyridine (**I**) differ only slightly from those found for 2-(2-pyridyl)pyrrole (**II**):  $\delta$  9.52 and 9.62 ppm (NH) and  $\delta$  6.76 and 6.69 ppm (3-H), respectively. We can conclude that the intramolecular hydrogen bond NH $\cdots$ N which stabilizes the conformation with *syn*

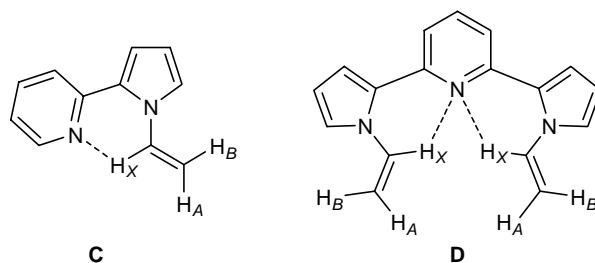


orientation of the pyrrole and pyridine rings in **II** is also formed in molecule **I**. Insofar as molecule **I** possesses two equivalent pyrrole rings, hydrogen atoms on the nitrogen in both pyrrole rings can equally participate in hydrogen bonding, i.e., bifurcated hydrogen bond  $\text{NH}\cdots\text{N}\cdots\text{HN}$  is formed in 2,6-bis(2-pyrrolyl)pyridine (**I**) (structure **B**).

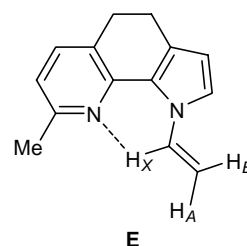
The difference in the chemical shifts of the NH proton between 2,6-bis(2-pyrrolyl)pyridine (**I**) and 2-(2-pyridyl)pyrrole (**II**) is as small as 0.1 ppm. Therefore, it is difficult to conclude whether the strength of the components of the  $\text{NH}\cdots\text{N}\cdots\text{HN}$  bifurcated hydrogen bond in molecule **I** is reduced relative to the strength of the ordinary  $\text{NH}\cdots\text{N}$  hydrogen bond in **II**. The N–H stretching vibration band in the IR spectrum of 2-(2-pyridyl)pyrrole (**II**) is displaced by 20–25  $\text{cm}^{-1}$  to lower frequencies (Table 2). 2,6-Bis(2-pyrrolyl)pyridine (**I**) shows in the IR spectrum only one N–H absorption band from the two pyrrole rings. These data suggest bifurcated mode of hydrogen bonding in molecule **I** rather than “pendular” oscillations of the N–H hydrogen atoms as a result of alternate formation of  $\text{NH}\cdots\text{N}$  hydrogen bonds involving different pyrrole fragments. In the latter case, two different absorption bands due to N–H stretching vibrations would be observed (free and H-bonded forms). The N–H stretching vibration frequency in the IR spectrum of **I** is higher by 8  $\text{cm}^{-1}$  than that in the spectrum of **II** (Table 2). This means some weakening of the  $\text{NH}\cdots\text{N}\cdots\text{HN}$  bifurcated hydrogen bond components in molecule **I**, as compared to the ordinary  $\text{NH}\cdots\text{N}$  hydrogen bond in compound **II** [8–11]. However, this effect is relatively small; otherwise, the high-frequency shift of the corresponding stretching vibration band could reach 100  $\text{cm}^{-1}$  [9].

1-Vinyl-2-(2-pyridyl)pyrrole (**VIII**) also exists as a conformer with *syn* orientation of the heterorings and *trans* orientation of the vinyl group with respect to the pyridine ring. This conformer is stabilized by the intramolecular hydrogen bond  $\text{CH}\cdots\text{N}$  between the  $\alpha$ -hydrogen atom of the vinyl group ( $\text{H}_X$ ) and pyridine nitrogen atom (structure **C**) [6, 12]. The formation of that hydrogen bond in molecule **VIII** induces a downfield shift of the  $\text{H}_X$  signal relative to the corresponding signal of structural analogs **IX–XI** ( $\Delta\delta = 1$  ppm) and increase of the direct  $^{13}\text{C}$ – $^1\text{H}$  coupling constant with  $\text{H}_X$  by 4 Hz (Table 3). A downfield shift of the  $\text{H}_X$  signal (by 1.4 ppm) and increase of the  $^1J(\text{C}^\alpha\text{--H}_X)$  value by 6 Hz are also observed in the spectrum of 2,6-bis(1-vinyl-2-pyrrolyl)pyridine (**VI**), as compared to 1,6-dimethyl-3,5-bis(1-vinyl-2-pyrrolyl)pyridine

(**VII**), indicating formation of bifurcated hydrogen bond  $\text{CH}\cdots\text{N}\cdots\text{HC}$  in molecule **VI** (structure **D**). This hydrogen bond ensures spatial proximity of the vinyl groups at the pyrrole rings in 2,6-bis(1-vinyl-2-pyrrolyl)pyridine (**VI**), which are oriented *trans* with respect to the pyridine ring. Each vinyl group is polarized due to  $p$ – $\pi$  conjugation; therefore, they possess a dipole moment. The dipole–dipole interaction between the two oppositely oriented dipoles in molecule **VI** is likely to induce some depolarization of the vinyl group, leading to the above noted downfield shift of the  $\text{C}^\beta$  signal by 1.2 ppm.



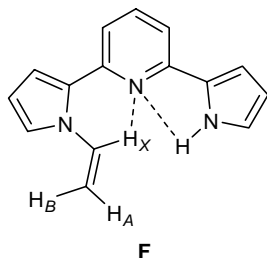
If the ordinary  $\text{CH}\cdots\text{N}$  hydrogen bond in 1-vinyl-2-(2-pyridyl)pyrrole (**VIII**) were considerably stronger than that of the components of the  $\text{CH}\cdots\text{N}\cdots\text{HC}$  bifurcated hydrogen bond in 2,6-bis(1-vinyl-2-pyrrolyl)pyridine (**VI**), the  $\text{H}_X$  proton in **VIII** would resonate in an appreciably weaker field and the coupling constant  $^1J(\text{C}^\alpha\text{--H}_X)$  would be much greater. This statement may be illustrated by comparing molecules **VI** and **VIII** with 1-vinyl-8-methyl-4,5-dihydro-1*H*-pyrrolo[3,2-*h*]quinoline (**XIV**). The pyrrole and pyridine rings in the molecule of the latter are fixed in one plane through the ethylene bridge, while the dihedral angle between the pyrrole and pyridine rings in 1-vinyl-2-(2-pyridyl)pyrrole (**VIII**) is  $\sim 20^\circ$  [12]. As a result, steric contraction of the H-chelate ring in molecule **XIV** makes the hydrogen bond stronger (the distance between the  $\text{H}_X$  and quinoline nitrogen atoms shortens, see structure **E**) [7, 13, 14]. As a result, the  $\text{H}_X$  signal is displaced by an additional 0.7 ppm, and the coupling constant  $^1J(\text{C}^\alpha\text{--H}_X)$  increases by 1.5 Hz (the latter assessment



should be performed with account taken of correlation (1) given in [6]).

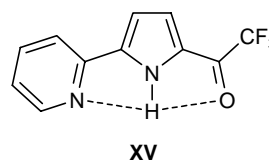
The observed differences in the  $H_X$  chemical shifts ( $\Delta\delta = 0.06$  ppm) and coupling constants  $^1J(C^\alpha-H_X)$  ( $\Delta J = 0.6$  Hz) between compounds **VI** and **VIII** are much less than those given above, and the character of their variation indicates some enhancement rather than weakening of the bifurcated hydrogen bond (Tables 2 and 3). Presumably, exclusively electrostatic nature of the  $CH\cdots N$  hydrogen bond [15–19] makes such interactions nonsaturable, i.e., both bifurcated and ordinary hydrogen bridges of that type are characterized by similar strengths.

The pyridine nitrogen atom in 2-(1-vinyl-2-pyrrolyl)-6-(2-pyrrolyl)pyridine (**XII**) is involved in hydrogen bonding with both NH hydrogen atom in the pyrrole ring and  $H_X$  in the vinylpyrrole fragment (structure **F**). This follows from downfield shifts of the corresponding proton signals in the  $^1H$  NMR spectrum of **XII** relative to signals from analogous protons in the spectra of compound **III–V** and **IX–XI** (Table 2). Thus the  $NH\cdots N\cdots HC$  bifurcated hydrogen bond in **XII** consists of nonequivalent components. In this case, the  $NH\cdots N$  hydrogen bond makes the  $CH\cdots N$  somewhat weaker. The  $H_X$  signal in the spectrum of **XII** suffers an appreciable upfield shift (by 0.2–0.3 ppm relative to **VI** and **VIII**; Table 2), and the coupling constant  $^1J(C^\alpha-H_X)$  decreases by 0.5–1.0 Hz (Table 3). These changes are unlikely to be induced by electronic effect of the pyrrole fragment in 2-(1-vinyl-2-pyrrolyl)-6-(2-pyrrolyl)pyridine (**XII**), for the chemical shifts of  $H_X$  in 2,6-dimethyl-3-(1-vinyl-2-pyrrolyl)-5-(2-pyrrolyl)pyridine (**XIII**) and 2,6-dimethyl-3,5-bis(1-vinyl-2-pyrrolyl)pyridine (**VII**) are almost equal ( $\delta$  6.50 and 6.52 ppm, respectively; Table 2). On the other hand, no reverse effect, i.e., weakening of the  $NH\cdots N$  hydrogen bond at the expense of  $CH\cdots N$ , is observed. The  $\delta(NH)$  values do not change in a regular mode in going from compound **XII** to pyrroles **I** and **II**, while the  $N-H$  stretching vibration frequency even decreases by 18 and 10  $cm^{-1}$ , respectively (Table 2). Obviously, the  $NH\cdots N$  bond is stronger than  $CH\cdots N$ ; therefore,



the effect of the former on the latter is stronger than vice versa.

Two kinds of bifurcated hydrogen bonds are possible. In molecules **I** and **VI**, the two hydrogen bonds involve proton-donor ( $N-H$  bonds) and proton-acceptor (pyridine nitrogen atom) functional groups. Bifurcated hydrogen bonds of another kind are formed with participation of one proton-acceptor group and two proton-donor moieties. The latter kind was revealed by us previously in 5-(2-pyridyl)-2-trifluoroacetylpyrrole (**XV**) where the  $N-H$  hydrogen atom interacts with both pyridine nitrogen atom and carbonyl oxygen atom of the trifluoroacetyl group [4].



It should be noted that the  $NH$  proton in 5-(2-pyridyl)-2-trifluoroacetylpyrrole resonates in a much weaker field ( $\delta$  10.48 ppm [4]) than those in pyrroles **I** and **II** ( $\Delta\delta = 0.8$  ppm), i.e., spectral effects induced by formation of different kinds of bifurcated hydrogen bonds are essentially different. The overall effect of the  $NH\cdots N$  and  $NH\cdots O$  hydrogen bonds in pyrrole **XV** on the chemical shift of the  $NH$  proton is approximately twice as strong as that produced by one  $NH\cdots N$  bond. Taking into account mainly electrostatic origin of these hydrogen bonds, doubling of the above effect may be interpreted in terms of superposition of the electric fields corresponding to the  $NH\cdots N$  and  $NH\cdots O$  interactions.

## EXPERIMENTAL

The  $^1H$  and  $^{13}C$  NMR spectra were recorded on a Bruker DPX-250 spectrometer at 250.1 and 62.9 MHz, respectively;  $CDCl_3$  was used as solvent ( $c = 5-10$  wt % for  $^{13}C$  and 0.1 wt % for  $^1H$ ), and HMDS, as internal reference; the parameters of pulse sequences were described in [4]. Two-dimensional HSQC and HMBIC experiments were performed using standard Bruker DPX-250 software optimized for  $^1J_{CH} = 160$  Hz and  $^nJ_{CH} = 8$  Hz.

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