Comparison of the Electronic and Steric Structures of 1-Vinyl- and 1-(Prop-1-en-1-yl)pyrroles according to the ^{1}H and ^{13}C NMR Data

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Abstract—According to the ^{1}H and ^{13}C NMR data, 1-isopropenylpyrroles are characterized by larger dihedral angles between the heteroring and exocyclic double bond planes, as compared to isostructural 1-vinylpyrroles, due to steric effect of the α-methyl group in the propenyl fragment. As a result, p–π conjugation with the propenyl group is weaker than with the vinyl group. The propenyl group in 1-isopropenylpyrrole having no other substituents in the heteroring is forced out from the heteroring plane, while the 1-vinylpyrrole molecule is planar. If substituents are present in positions *2* and *5* of the pyrrole ring, the propenyl group on the nitrogen atom becomes orthogonal with respect to the pyrrole ring plane, so that no p–π conjugation is possible. The steric structures of (*E*)-1-(prop-1-en-1-yl)pyrrole and (*Z*)-1-(prop-1-en-1-yl)pyrrole are different: the propenyl group in the former is turned relative to the heteroring plane, while the latter molecule is planar.

The steric and electronic structures of 1-vinylpyrroles were studied in detail by ^{1}H and ^{13}C NMR spectroscopy [1–6]. It was shown that π systems of the vinyl group and pyrrole ring efficiently interact with each other via p–π conjugation mechanism, which leads to excess shielding of the β-carbon atom of the vinyl group. The vinyl group and pyrrole ring in 1-vinylpyrrole lie in one plane, so that the maximal degree of p–π conjugation is attained. The presence of alkyl groups in the 2-position of the pyrrole ring forces the vinyl group to go out from the pyrrole ring plane; as a result, p–π conjugation with the vinyl group weakens, and the degree of shielding of its β-carbon atom decreases. The larger the alkyl group in position *2* of pyrrole ring, the greater the deviation of the vinyl group from the pyrrole ring plane and the weaker the p–π conjugation. If substituents are present in both 2- and 5-positions of the pyrrole ring, deviation of the vinyl group from the pyrrole ring plane becomes especially strong, and p–π conjugation with the vinyl group is disrupted almost completely [1–6]. The aromatic ring in 2-aryl-1-vinylpyrroles is involved in conjugation, and electronic effect of a substituent in the

para position of the 2-aryl group is transmitted to the vinyl group through the pyrrole ring [7–9].

Distortion of coplanarity between the vinyl group and pyrrole ring is reflected in a number of ^{1}H and ^{13}C NMR parameters, including deshielding of the β-carbon atom [1–6]. In addition, the geminal coupling constants between the H_A and H_B vinyl protons increase [3, 5], while the long-range coupling constants between the vinyl group protons and protons in the pyrrole ring [3, 5] and the direct [13]C–[1]H coupling constants of the C^β carbon atom change in opposite directions [9, 10].

We recently synthesized a new series of 1-(prop-1-en-1-yl)pyrroles [11]. Even at first glance, parameters of the ^{1}H and ^{13}C NMR spectra of these compounds revealed a strong dependence of the efficiency of p–π conjugation with the olefinic fragment on the presence of substituents in the pyrrole ring. With a view to gain a deeper insight into the electronic and steric structures of 1-(prop-1-en-1-yl)pyrroles we performed a detailed analysis of the ^{1}H and ^{13}C NMR parameters of a wider series (than that described in [11]) of substrates (compounds **I–XV**) and compared the obtained data with
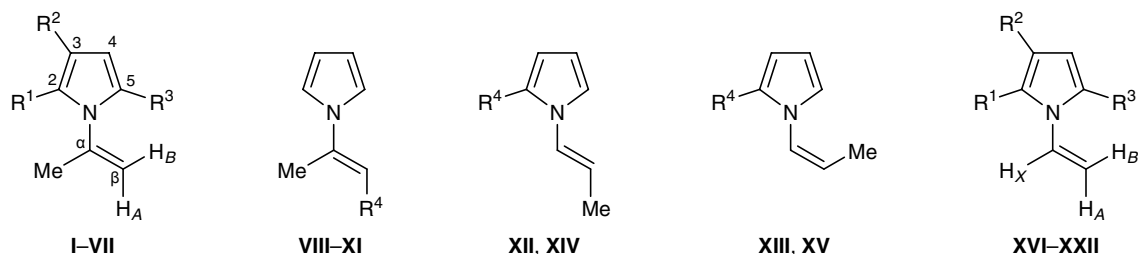
I, XVI, $R^1 = R^2 = R^3 = H$; **II, XVII**, $R^1 = R^2 = Me$, $R^3 = H$; **III, XVIII**, $R^1 = R^2 = R^3 = Me$; **IV, XIX**, $R^1R^2 = (CH_2)_4$, $R^3 = H$; **V, XX**, $R^1R^2 = (CH_2)_4$, $R^3 = Me$; **VI, XXI**, $R^1 = Ph$, $R^2 = R^3 = H$; **VII, XXII**, $R^1R^2 = (CH)_4$, $R^3 = H$; **VIII**, $R^4 = Ph$; **IX**, $R^4 =$ 4-t-BuC$_6$H$_4$; **X**, $R^4 =$ 4-MeOC$_6$H$_4$; **XI**, $R^4 =$ MeO; **XII, XIII**, $R^4 = H$; **XIV, XV**, $R^4 = Ph$.

those typical of isostructural 1-vinylpyrroles **XVI–XXII**.

The ^{13}C and ^{1}H parameters of pyrroles **I–XXII** are collected in Tables 1 and 2, and the ^{13}C–^{1}H coupling constants are given in Table 3. Table 4 contains ^{13}C chemical shifts of reference compounds [12]: ethylene, propene, styrene, and methoxyethene. The ^{1}H and ^{13}C NMR signals were assigned on the basis of the data obtained using ^{1}H–^{1}H 2M COSY and NOESY and heteronuclear ^{1}H–^{13}C 2M HSQC and HMBC techniques. The ^{1}H and ^{13}C NMR signals of the pyrrole ring were assigned according to the scheme described in [13]. Signals from methyl groups at the exocyclic double bond in the ^{1}H NMR spectra of pyrroles having other methyl groups were identified by the presence in their HMBC spectra of a cross peak with the olefinic carbon atoms through two bonds. Likewise, signals from protons of the methyl groups in positions *2* and *3* of pyrroles **II** and **XVII** were assigned on the basis of cross peaks with C^2 and C^3 through two bonds in the HMBC spectra. The presence of a cross peak with 4-H in the NOESY spectra of pyrroles **III** and **XVIII** allowed us to distinguish signals from protons in the 3- and 5-methyl groups from the 2-Me signal. All methyl group signals in the ^{13}C NMR spectra were identified by correlation with the corresponding proton signals in the HSQC spectra. The 4-H and 7-H protons in the fused cyclohexene ring of tetrahydroindoles **IV, V, XIX**, and **XX** gave rise to off-diagonal peaks with 3-H and protons of the olefinic fragment (H$_A$, H$_B$, H$_X$, or CH$_3$), respectively. The 5-H and 6-H protons in the same ring gave cross peaks through three bonds with C^9 and C^8, respectively, in the HMBC spectra. The corresponding carbon atoms (C^4–C^7) of tetrahydroindoles **IV, V, XIX**, and **XX** showed in the HSQC NMR spectra correlations with protons attached thereto.

Compounds **VIII–XI** may have either *Z*- or *E*-isomer structure. The presence of a cross peak between the olefinic proton and 2-H (or 5-H) in the NOESY

spectrum unambiguously indicated that these compounds exist as *E* isomers (structure **A**). The configuration of pyrroles **XII–XV** was determined on the basis of vicinal coupling constants between the olefinic protons, which were equal to 14.2 and 14.0 Hz for **XII** and **XIV** and 9.1 and 8.6 Hz for **XIII** and **XV**, respectively. Therefore, compounds **XII** and **XIV** were assigned the structure of *E* isomers, while compounds **XIII** and **XV**, *Z* isomers.

A
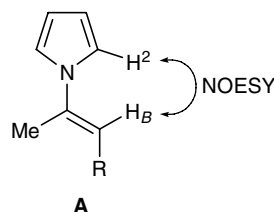
It is seen (Table 1) that the signal from the β-carbon atom in the propenyl group of 1-isopropenylpyrrole (**I**) is displaced strongly upfield relative to the corresponding propene signal. This means that *p*–π conjugation between the pyrrole ring and propenyl group is fairly effective. However, the difference $\Delta\delta_C = 17.6$ ppm for 1-isopropenylpyrrole (**I**) is considerably smaller than that for 1-vinylpyrrole (**XVI**) ($\Delta\delta_C = 26.4$ ppm). Even the overall effect including *p*–π conjugation with the pyrrole ring and σ–π conjugation with the methyl group in **I** induces smaller shift of the β-carbon signal ($\Delta\delta_C = 25.4$ ppm; Table 1) as compared to 1-vinylpyrrole (**XVI**). These findings indicate weakening of *p*–π conjugation with the exocyclic double bond in 1-isopropenylpyrrole (**I**) as a result of distortion of coplanarity between the double bond and heteroring planes


B
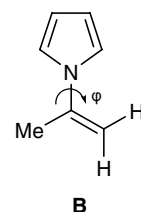
(increase of dihedral angle φ, as shown in structure **B**) due to steric effect of the α-methyl group in the propenyl fragment.

The signal from the β-carbon atom of the propenyl group in 1-isopropenyl-2,3-dimethylpyrrole (**II**) is located in a considerably weaker field ($\Delta\delta_C = 10.4$ ppm) relative to the corresponding signal of 1-isopropenyl-pyrrole (**I**), whereas no such difference is observed in going from 1-vinylpyrrole (**XVI**) to 2,3-dimethyl-1-vinylpyrrole (**XVII**) (Table 1). Spatial interaction between the methyl groups in the α-position of the propenyl group and in position *2* (or *5*) of the pyrrole ring leads to a strong deviation of the propenyl group from the heteroring plane and considerably weakens *p*–π conjugation between these fragments; therefore, excess shielding of the propenyl β-carbon atom in pyrrole **II** is as small as 7.1 ppm. The position of the C^β signal in the ^{13}C NMR spectrum of 1-isopropenyl-2,3,5-trimethylpyrrole (**III**) is even more downfield, so that it approaches the position of the corresponding carbon signal in the spectrum of propene (Table 1). The absence of excess shielding of C^β in **III** suggests complete distortion of *p*–π conjugation in its molecule, which is possible when the propenyl and heteroring planes are mutually orthogonal. 2,3,5-Trimethyl-1-vinylpyrrole (**XVIII**) retains fairly effective *p*–π conjugation with the vinyl group (excess shielding of the vinyl β-carbon atom is 19.2 ppm); therefore, the dihedral angle between the vinyl group plane and the pyrrole ring is relatively small. Thus, methyl group in the α-position of the vinyl group exerts a very strong effect on the steric and electronic structures of 1-propenylpyrroles.

Shielding of the β-carbon atom in 1-isopropenyl-4,5,6,7-tetrahydroindole (**IV**) and 1-isopropenylindole (**VII**) is slightly greater, while in 1-isopropenyl-2-phenylpyrrole (**VI**) smaller, than in 1-isopropenyl-2,3-dimethylpyrrole (**II**). The observed differences may originate from both electronic effects of substituents in the pyrrole ring and change of the dihedral angle between the propenyl group and pyrrole ring planes. To distinguish between these two factors, analysis of the ^1H NMR spectra is necessary (see below). Excess shielding of the β-carbon atom in 1-isopropenyl-2-methyl-4,5,6,7-tetrahydroindole (**V**), as well as in 1-isopropenyl-2,3,5-trimethylpyrrole (**III**), is almost absent (Table 1). Here, spatial interaction between the substituents in positions *2* and *5* of the pyrrole ring, on the one hand, and methyl group at the α-carbon atom, on the other, leads to orthogonal orientation of the propenyl group plane with respect to the pyrrole ring.

Analysis of the two-dimensional NOESY spectra allowed us to determine preferential orientation of the propenyl group in 1-isopropenyl-2,3-dimethylpyrrole (**II**) and 1-isopropenyl-4,5,6,7-tetrahydroindole (**IV**). The NOESY spectra contained cross peaks between protons of the α-methyl group and 5-H (2-H) and between H_B and 2-CH$_3$ in pyrrole **II** and between H_B and 7-H in tetrahydroindole **IV**. These findings indicate *trans* orientation of the α-methyl group with respect to the substituent in the pyrrole ring (structure **C**); obviously, mutual arrangement of the above fragments in molecules **II** and **IV** is determined by steric repulsion.

C
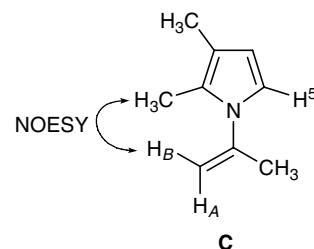
Excess shielding of the β-carbon atom in 1-(1-methyl-2-phenylvinyl)pyrrole (**VIII**) due to *p*–π conjugation with the olefinic fragment is estimated at 20.3 ppm relative to C^α in styrene; moreover, the effect is transmitted to the phenyl ring, leading to additional shielding of the *para*-carbon atom by 2.2 ppm (Table 1). On the other hand, conjugation between the phenyl ring and exocyclic double bond in molecule **VIII** induces only 4.8-ppm upfield shift of the C^α signal (relative to the C^α signal of 1-isopropenylpyrrole), while the difference in the chemical shifts of C^β between styrene and ethylene is 10.1 ppm (Tables 1, 4). Thus, strong *p*–π conjugation between the pyrrole ring and the exocyclic double bond inhibits π-donor effect of the phenyl group on the double bond. This is the reason why the electronic effect of the methoxy group on the double bond through the benzene ring in pyrrole **X** is very weak: the upfield shift of the C^α signal in going from pyrrole **VIII** to **X** is as small as 1 ppm (Table 1).

Weakening of *p*–π conjugation with the double bond is clearly illustrated by the NMR data for 1-(2-methoxy-1-methylvinyl)pyrrole (**XI**). The upfield shift of the β-carbon signal due to joint effects of *p*–π conjugation with the pyrrole ring and σ–π conjugation in molecule **XI** is only 12.9 ppm (relative to the C^α signal of methoxyethene) against 25.4 ppm for 1-isopropenylpyrrole (**I**); *p*–π conjugation with the methoxy group induces an upfield shift of the α-carbon signal

Table 1. ^{13}C NMR parameters of 1-propenyl- and 1-vinylpyrroles **I–XXII**[a]

Comp. no.	Chemical shift δ_C, ppm						
	C^α	C^β	C^2	C^3	C^4 (C^9)	C^5 (C^8)	CH_3, CH_2
I	140.69	97.93 (–17.6)[b] (–25.4)[d]	118.24	109.56 (–0.7)[c]	109.56 (–0.7)[c]	118.24	20.39 (α-CH$_3$)
II	142.19	108.37 (–7.1)[b]	124.49	116.17	109.34	118.15	22.70 (α-CH$_3$), 10.88 (2-CH$_3$), 11.49 (3-CH$_3$)
III	142.00	115.11 (–0.4)[b]	123.12	113.58	107.40	125.94	22.97 (α-CH$_3$), 10.00 (2-CH$_3$), 11.05 (3-CH$_3$), 12.14 (5-CH$_3$)
IV	141.15	105.24 (–10.3)[b]	118.27	107.39	119.06	127.78	22.37 (α-CH$_3$), 23.35 (4-CH$_2$), 23.88 (5-CH$_2$), 23.35 (6-CH$_2$), 24.22 (7-CH$_2$)
V	141.33	114.28 (–1.2)[b]	126.71	105.36	116.44	126.71	22.88 (α-CH$_3$), 12.25 (2-CH$_3$), 23.02 (4-CH$_2$), 23.85 (5-CH$_2$), 23.65 (6-CH$_2$), 22.25 (7-CH$_2$)
VI	143.34	110.14 (–5.4)[b]	133.08	110.50	108.34	123.58	22.38 (α-CH$_3$)
VII	140.85	105.73 (–9.8)[b]	126.33	103.11	129.58	135.61	22.16 (α-CH$_3$)
VIII	135.91 (–4.8)[e]	116.44 (–20.3)[f]	118.70	109.59	109.59	118.70	16.83 (α-CH$_3$)
IX	135.48	116.48	118.74	109.50	109.50	118.74	17.00 (α-CH$_3$), 34.58 (t-Bu, C), 31.38 (t-Bu, CH$_3$)
X	134.86	116.38	118.75	109.39	109.39	118.75	16.94 (α-CH$_3$), 55.32 (OCH$_3$)
XI	119.76 (–20.9)[e]	140.66 (–12.9)[g]	119.76	108.58	108.58	119.76	14.14 (α-CH$_3$), 60.13 (OCH$_3$)
XII	128.21 (–4.9)[c]	109.52 (–24.1)[b]	118.53	109.65 (–0.6)[c]	109.65 (–0.6)[c]	118.53	15.02 (β-CH$_3$)
XIII	127.15 (–5.9)[c]	113.95 (–19.6)[b]	121.11	108.79 (–1.5)[c]	108.79 (–1.5)[c]	121.11	12.84 (β-CH$_3$)
XIV	127.02	112.94 (–20.7)[b]	133.75	109.55	109.43	119.60	15.25 (β-CH$_3$)
XV	127.47	123.25 (–10.3)[b]	134.33	108.86	108.78	118.53	12.75 (β-CH$_3$)
XVI	133.14	96.86 (–26.4)[g]	118.77	110.29	110.29	118.77	
XVII	130.82	96.75 (–26.5)[d]	124.77	116.23	111.33	114.63	9.57 (2-CH$_3$), 11.22 (3-CH$_3$)
XVIII	131.22	104.12 (–19.2)[d]	123.99	115.01	109.47	126.94	11.13 (2-CH$_3$), 11.06 (3-CH$_3$), 13.63 (5-CH$_3$)
XIX	130.19	95.73 (–27.6)[d]	114.85	109.27	118.89	127.54	23.00 (4-CH$_2$), 23.40 (5-CH$_2$), 23.11 (6-CH$_2$), 21.77 (7-CH$_2$)
XX	130.46	101.52 (–21.8)[d]	127.40	107.39	118.14	127.06	23.05 (4-CH$_2$), 23.29 (5-CH$_2$), 23.71 (6-CH$_2$), 23.93 (7-CH$_2$), 13.37 (2-CH$_3$)
XXI	132.08	98.81 (–24.5)[d]	134.39	110.15	110.12	118.35	
XXII	129.56	96.25 (–27.0)[d]	123.35	104.89	135.50	129.33	

Table 1. (Contd.)

a Chemical shifts of the aromatic carbon atoms, δ_C, ppm: **VI**: 133.82 (C^i), 127.53 (C^o), 128.30 (C^m), 123.58 (C^p); **VII**: 121.18 (C^4), 122.35 (C^5), 120.36 (C^6), 112.02 (C^7); **VIII**: 136.50 (C^i), 129.07 (C^o), 128.36 (C^m), 126.58 (C^p); **IX**: 133.58 (C^i), 128.81 (C^o), 125.32 (C^m), 149.57 (C^p); **X**: 128.92 (C^i), 130.22 (C^o), 113.83 (C^m), 158.92 (C^p); **XIV**: 132.98 (C^i), 129.16 (C^o), 128.46 (C^m), 126.71 (C^p); **XV**: 133.19 (C^i), 129.16 (C^o), 128.35 (C^m), 126.71 (C^p); **XXI**: 132.52 (C^i), 128.49 (C^o), 128.35 (C^m), 127.28 (C^p); **XXII**: 121.13 (C^4), 122.69(C^5), 120.77 (C^6), 109.53 (C^7).

b Relative to propene.

c Relative to 1-vinylpyrrole.

d Relative to ethylene.

e Relative to 1-(1-methylvinyl)pyrrole (**I**).

f Relative to styrene.

g Relative to methoxyethene.

by 20.9 ppm relative to the C^α signal of **I**, whereas the corresponding difference between methoxyethene and ethylene is 37.3 ppm (Table 1).

In the ^{13}C NMR spectrum of (*E*)-1-(prop-1-en-1-yl)pyrrole (**XII**), the chemical shift of the β-carbon

atom is lesser by 24.1 ppm than the chemical shift of C^α in propene (due to *p*–π conjugation). The difference is almost the same as that found for 1-vinylpyrrole (**XVI**) ($\Delta\delta_C = 26.4$ ppm). A slightly weaker *p*–π interaction in pyrrole **XII** compared to **XVI** may be

Table 2. ^1H NMR parameters of 1-propenyl- and 1-vinylpyrroles **I–XXII**[a]

Comp. no.	Chemical shift δ, ppm								
	$\Delta\delta$	H_A	H_B	H_X	2-H	3-H	4-H	5-H	CH₃, CH₂
I	0.37	4.54	4.91		6.95	6.21	6.21	6.95	2.19 (α-CH₃)
II	–0.08	4.94	4.82				5.96	6.57	2.09 (α-CH₃), 2.14 (2-CH₃), 2.02 (3-CH₃)
III	–0.36	5.28	4.92				5.68		1.95 (α-CH₃), 2.06 (2-CH₃), 1.97 (3-CH₃), 2.12 (5-CH₃)
IV	–0.02	4.80	4.78		6.64	5.96			2.12 (α-CH₃), 2.52 (4-H), 1.75 (5-H, 6-H), 2.59 (7-H)
V	–0.32	5.22	4.90			5.96			1.98 (α-CH₃), 2.46 (4-H, 7-H), 1.74 (5-H, 6-H)
VI	–0.02	4.97	4.95		6.30	6.22	6.78		2.12 (α-CH₃)
VII	0.10	5.06	5.16		7.21	6.55			1.98 (α-CH₃), 2.16 (2-CH₃)
VIII			6.59		7.02	6.26	6.26	7.02	2.33 (α-CH₃)
IX			6.56		7.02	6.25	6.25	7.02	2.34 (α-CH₃), 1.32 (*t*-Bu)
X			6.53		7.01	6.25	6.25	7.01	2.31 (α-CH₃), 3.82 (OCH₃)
XI			6.30		6.72	6.17	6.17	6.72	2.06 (α-CH₃), 3.64 (OCH₃)
XII			5.63	6.61	6.79	6.16	6.16	6.79	1.77 (β-CH₃)
XIII		5.21		6.59	6.80	6.21	6.21	6.80	1.84 (β-CH₃)
XIV			5.73	6.66		6.24	6.24	6.99	1.76 (β-CH₃)
XV		5.42		6.52		6.32	6.27	6.86	1.80 (β-CH₃)
XVI	0.47	4.54	5.01	6.72	6.81	6.18	6.18	6.81	
XVII	0.43	4.57	5.00	6.82			6.00	6.87	2.14 (2-CH₃), 2.00 (3-CH₃)
XVIII	0.15	4.86	5.01	6.71			5.72		2.16 (2-CH₃), 1.96 (3-CH₃), 2.23 (5-CH₃)
XIX	0.45	4.52	4.97	6.74	6.83	5.99			2.46 (4-CH₂), 1.70 (5-H), 1.79 (6-H), 2.55 (7-H)
XX	0.22	4.75	4.97	6.72		5.70			2.25 (2-CH₃), 2.44 (4-H), 1.75 (5-H₂), 1.81 (6-H), 2.61 (7-H)
XXI	0.49	4.63	5.12	6.86		6.23	6.26	7.07	
XXII	0.43	4.73	5.16	7.20	7.40	6.66			

a Chemical shifts of aromatic protons, δ, ppm: **VI**: 7.42 (*o*-H), 7.32 (*m*-H), 7.22 (*p*-H); **VII**: 7.62 (4-H), 7.21 (5-H), 7.11 (6-H), 7.62 (7-H); **VIII**: 7.27 (*o*-H), 7.35 (*m*-H), 7.23 (*p*-H); **IX**: 7.23 (*o*-H), 7.37 (*m*-H); **X**: 7.22 (*o*-H), 6.90 (*m*-H); **XIV**: 7.39 (*o*-H), 7.35 (*m*-H), 7.29 (*p*-H); **XV**: 7.45 (*o*-H), 7.42 (*m*-H), 7.29 (*p*-H); **XXI**: 7.34 (*o*-H), 7.32 (*m*-H), 7.27 (*p*-H); **XXII**: 7.71 (4-H), 7.30 (5-H), 7.27 (6-H), 7.45 (7-H).

Table 3. Direct coupling constants $^{13}C–^{1}H$ (Hz) in the ^{13}C NMR spectra of 1-propenyl- and 1-vinylpyrroles **I–XIII** and **XVI–XXII**

Compound no.	ΔJ	$C^\beta–H_A$	$C^\beta–H_B$	$C^\alpha–H_X$	$C^2–H$	$C^3–H$	$C^4–H$	$C^5–H$
I	4.9	161.9	157.0		184.8	171.4	171.4	184.8
II	0	158.8	158.8				167.8	184.0
III	–2.0	157.3	159.3				165.9	
IV	0	158.7	158.7		184.2	168.2		
V	–1.4	157.6	159.0			166.0		
VI	0	159.5	159.5			170.4	171.4	186.0
VII	0.6	159.5	158.9		183.3	173.4		
VIII			153.4		184.7	171.0	171.0	184.7
IX			152.6		185.2	171.2	171.2	185.2
X			155.4		185.0	171.0	171.0	185.0
XI			177.9		184.5	170.5	170.5	184.5
XII			151.9	172.8	184.7	171.0	171.0	184.7
XIII		156.8		176.7	185.2	171.0	171.0	185.2
XVI	7.0	164.0	157.0	174.2	185.2	171.4	171.4	185.2
XVII	6.5	163.2	156.7	173.7			169.1	184.5
XVIII	2.7	161.5	158.8	172.0			167.1	
XIX	6.2	163.1	156.9	172.1	184.5	168.7		
XX	2.3	161.1	158.6	171.4		167.4		
XXI	6.5	163.5	157.0	176.1			171.1	171.7	185.7
XXII	7.1	164.1	157.0	173.0				

rationalized in terms of the opposite effect of donor σ–π interaction with the β-methyl group in the propenyl fragment. Taking into account the lack of steric repulsion between the pyrrole ring and fairly distant *trans*-methyl group, coplanar arrangement of the pyrrole ring and propenyl group in (*E*)-1-(prop-1-en-1-yl)pyrrole (**XII**) may be assumed.

In going from (*E*)-1-(prop-1-en-1-yl)pyrrole (**XII**) to isomeric (*Z*)-1-(prop-1-en-1-yl)pyrrole (**XIII**), the β-carbon atom becomes less shielded ($\Delta\delta_C = 4.4$ ppm). The reason is partial rupture of *p*–π conjugation as a result of deviation of the propenyl group from the

Table 4. ^{13}C NMR chemical shifts of substituted ethenes[a]

Compound	δ_C, ppm	
	C^α	C^β
$CH_2=CH_2$	123.3	123.3
$CH_3CH=CH_2$	133.6	115.5
$PhCH=CH_2$	136.7	113.2
$CH_3OCH=CH_2$	153.6	86.0

[a] Data of [12].

pyrrole ring plane due to steric effect of the *cis*-β-methyl group. As the *p*–π conjugation with the propenyl group in molecule **XIII** weakens, σ–π interaction with the β-methyl group becomes stronger, and the C^α signal shifts upfield by 1 ppm relative to the corresponding signal of **XII** (Table 1).

Some deshielding of the C^β atom in (*E*)-2-phenyl-1-(prop-1-en-1-yl)pyrrole (**XIV**) compared to (*E*)-1-(prop-1-en-1-yl)pyrrole (**XII**) is similar to that observed in going from 2-phenyl-1-vinylpyrrole (**XXI**) to 1-vinylpyrrole (**XVI**). However, the C^β atom in (*Z*)-2-phenyl-1-(prop-1-en-1-yl)pyrrole (**XV**) is deshielded much more strongly than in its isomer (**XIV**) ($\Delta\delta_C = 10.3$ ppm). Steric interaction between the β-methyl group and 2-phenyl substituent leads to considerable deviation of the propenyl group from the heteroring plane.

Change of the orientation of the propenyl group relative to the pyrrole ring is reflected in the ^{1}H NMR spectra (Table 2), where different effects of the magnetically anisotropic pyrrole ring on protons in the propenyl group are observed. In the ^{1}H NMR spectrum

of 1-isopropenylpyrrole (**I**), which is characterized by a small dihedral angle (φ) between the propenyl group and pyrrole ring planes, the chemical shift of protons in the α-methyl group is δ 2.19 ppm. Increase in the angle φ in going to pyrroles **II**, **IV**, and **VI** is accompanied by upfield shift of the α-methyl proton signal to δ 2.09–2.12 ppm, and the corresponding signal of **III** and **V** with orthogonal orientation of the propenyl group and heteroring appears at δ 1.95–1.98 ppm.

The chemical shifts of the β-protons in the vinyl or propenyl group are sensitive to the steric structure. Distortion of the planar structure and hence rupture of p–π conjugation induces downfield shift of the *trans*-β-proton signal (H_A) (as well as of the C^β signal), while the *cis*-β-proton signal (H_C) shifts upfield due to anisotropic effect of the pyrrole ring [14]. As the exocyclic double bond deviates from the heteroring plane, the difference in the chemical shifts of H_B and H_A ($\Delta\delta_{AB} = \delta H_B - \delta H_A$) decreases, and it becomes negative at large dihedral angles φ [15, 16]. The parameter $\Delta\delta_{AB}$ for 1-isopropenylpyrrole (**I**) insignificantly differs from that found for 1-vinylpyrrole (**XVI**) (0.37 and 0.47 ppm, respectively; Table 2). However, in going to 1-isopropenyl-2,3-dimethylpyrrole (**II**), the $\Delta\delta_{AB}$ value decreases so strongly that it becomes negative (–0.08 ppm). The difference between $\Delta\delta_{AB}$ values for pyrroles **II** and **I** exceeds the whole range of variation of $\Delta\delta_{AB}$ for 1-vinylpyrroles **XVI–XXII**, indicating considerable acoplanarity of the propenyl group and pyrrole ring. It should be noted that $\Delta\delta_{AB}$ for 1-isopropenylindole (**VII**) is appreciably greater than those for 2-substituted isopropenylpyrroles **II**, **IV**, and **VI**. Presumably, steric effect of the fused benzene ring on the propenyl group is much weaker than the effects of alkyl substituents; therefore, the corresponding deviation of the propenyl group from the heteroring plane is much smaller. Compounds **III** and **V** in which the propenyl group is orthogonal to the pyrrole ring are characterized by large negative values of $\Delta\delta_{AB}$ (–0.36 and –0.32 ppm, respectively; Table 2).

The 7-H signal in the ¹H NMR spectrum of 1-isopropenyl-2-methyl-4,5,6,7-tetrahydroindole (**V**) is displaced upfield by 0.09–0.15 ppm relative to the corresponding signals of tetrahydroindoles **IV**, **XIX**, and **XX**. A probable reason is that the 7-H proton in **IV**, **XIX**, and **XX** is deshielded due to magnetically anisotropic effect of the vinyl or propenyl fragment; the propenyl group in **V** is oriented orthogonally to the heteroring plane, so that it does not exert deshielding effect on 7-H.

We previously showed that direct ¹³C–¹H coupling constants for the vinyl β-carbon atom are sensitive to the steric structure and that they depend on the dihedral angle (φ) between the vinyl group and heteroring planes [10, 16]. The coupling constant of C^β with *trans*-β-H decreases, while that with *cis*-β-H increases, as the angle φ rises; correspondingly, the difference $\Delta J = {}^1J(C^\beta–H_A) - {}^1J(C^\beta–H_B)$ decreases [10, 16]. The ΔJ value for 1-isopropenylpyrrole (**I**) is 4.9 Hz (Table 3). In going to 2-substituted pyrroles **II** and **VI**, tetrahydroindole **IV**, and indole **VII**, ΔJ decreases to 0–0.6 Hz in parallel with considerable increase of the dihedral angle φ. The difference ΔJ for indole **VII** is somewhat larger than the corresponding parameters of compounds **II**, **IV**, and **VI**, indicating that molecule **VII** is more planar. Orthogonal orientation of the propenyl group and heteroring in 2,5-substituted pyrrole **III** and 2-substituted tetrahydroindol **V** is characterized by negative values of ΔJ. The range of variation of ΔJ for propenyl-substituted compounds **I–VII** ($\Delta\Delta J = 6.9$ Hz) exceeds that for vinyl-substituted analogs **XVI–XXII** ($\Delta\Delta J = 4.8$ Hz), in keeping with the wider range of variation of the dihedral angle between the planes of the propenyl group and heteroring, as compared to vinyl group.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were recorded on a Bruker DPX-250 spectrometer (250.1 and 62.9 MHz, respectively) using CDCl₃ as solvent ($c = 5$–10 wt %) and hexamethyldisiloxane as internal reference. The pulse sequence parameters for recording the ¹H and ¹³C NMR spectra were reported in [17]. Two-dimensional COSY, NOESY, HSQC, and HMBC spectra were measured using standard built-in programs optimized for ${}^1J_{CH} = 160$ Hz (HSQC) and ${}^nJ_{CH} = 8$ Hz (HMBC). The IR spectra were obtained on a Bruker IFS 25 spectrometer from samples prepared as thin films (liquid substances) or KBr pellets (crystalline substances). The mass spectra of compounds **XVIII** and **XX** (electron impact, 60 eV) were recorded on an LKB-2091 GC–MS system (38-m SE-54 capillary column, injector temperature 250°C, oven temperature programming from 70 to 200°C at 10 deg/min; ion source temperature 240°C). Compound **XI** was isolated by preparative gas–liquid chromatography on a PAKhV-07 instrument equipped with a 5-m×10-mm column; stationary phase 5% of XE-60 on Chromaton N-AW-HMDS; thermal conductivity detector; carrier gas helium; oven temperature 100°C, detector temperature 200°C, injector temperature 230°C.

1-Isopropenylpyrroles **I–VI** were synthesized by reactions of the corresponding NH-pyrroles with propyne and allene according to the procedure described in [11]. 1-(Prop-1-en-1-yl)pyrroles **XII** and **XIII** were obtained by isomerization of 1-allylpyrrole in the system KOH–DMSO [18]. 1-Vinylpyrrole (**XVI**) and its derivatives **XVIII** and **XX** were prepared by vinylation of the corresponding NH-pyrroles with acetylene in the system KOH–DMSO under atmospheric pressure [19]. Compounds **XVIII** and **XX** were not described previously.

2,3,5-Trimethyl-1-vinyl-1*H*-pyrrole (XVIII) was obtained from 2,3,5-trimethyl-1*H*-pyrrole [20] and acetylene (120–126°C, 2 h). Yield 51%, colorless liquid, bp 73°C (7 mm), n_D^{24} = 1.5201, purity 95%. IR spectrum, ν, cm^{-1}: 3122 w, 3088 w, 2972, 2921 s, 2862 s, 2737 w, 1642 s, 1602, 1424 s, 1397 s, 1535, 1376, 1341 s, 1302 s, 1167 w, 1140 w, 1111 w, 1074 w, 1037 w, 1006 w, 969 s, 866 s, 782 s, 717, 694 w, 631, 575 w, 510 w. Mass spectrum, *m/z* (I_{rel}, %): 135 (100) [*M*]$^+$, 134 (100), 120 (46), 118 (13), 108 (13), 106 (15), 93 (15), 91 (24), 79 (43), 77 (30), 67 (48), 65 (33), 53 (20), 51 (17), 42 (65), 39 (63).

2-Methyl-1-vinyl-4,5,6,7-tetrahydro-1*H*-indole (XX) was obtained from 2-methyl-4,5,6,7-tetrahydro-1*H*-indole [20] and acetylene (115–125°C, 2 h). Yield 49%, light yellow liquid, bp 105°C (6 mm), n_D^{21} = 1.5534, purity 95%. IR spectrum, ν, cm^{-1}: 3123 w, 3087 w, 3049 w, 2972, 2969, 2930, 2843 s, 1642 s, 1600, 1535 s, 1429 s, 1396 s, 1382, 1347, 1328, 1290 s, 1254, 1238, 1205 w, 1154, 1101, 1074 w, 1058 w, 1034 w, 993, 968 s, 938, 858 s, 779 s, 724 w, 693, 639, 604 w, 580. Mass spectrum, *m/z* (I_{rel}, %): 161 (89) [*M*]$^+$, 147 (22), 134 (100), 117 (1), 91 (13), 77 (8), 65 (7), 40 (6), 33 (6), 28 (32).

Substituted 1-vinylpyrroles **XVII**, **XIX**, and **XXI** were synthesized by the Trofimov reaction from the corresponding ketone oximes and acetylene [6, 21]. 1-Vinylindole was prepared by vinylation of indole with acetylene in aqueous dioxane in the presence of 30% KOH under pressure [22]. Previously unknown compounds **VIII–XI** were synthesized by reaction of pyrrole with prop-2-yn-1-ylbenzene, *para*-substituted prop-2-yn-1-ylbenzenes, and 3-methoxypropyne in the system KOH–DMSO [23].

1-[(*E*)-1-Methyl-2-phenylvinyl]-1*H*-pyrrole (VIII). Pyrrole, 3.35 g (50 mmol), was added to a suspension of 3.25 g (50 mmol) of powdered KOH·0.5H$_2$O in 25 ml of DMSO containing less than 0.2%

of water. The mixture was heated to 120–127°C, a solution of 5.8 g (50 mmol) of prop-2-yn-1-ylbenzene in 5 ml of DMSO was added dropwise under stirring over a period of 30 min, the mixture was cooled and diluted with water, and the precipitate was filtered off, repeatedly washed with water (until neutral washings), and dried. We thus isolated 6.75 g of compound **VIII**. The aqueous phase was extracted with 4 portions of diethyl ether, the extracts were combined, washed with water, and dried over MgSO$_4$, the solvent was removed, and the residue was evacuated at a residual pressure of 2 mm to isolate an additional portion of **VIII**, 1.54 g, as brown crystals. The two portions of the product were combined and recrystallized from hexane to obtain 5.77 g of pure compound **VIII** as colorless crystals with mp 78°C. IR spectrum, ν, cm^{-1}: 3132 w, 3103 w, 3045 w, 3022 w, 3005 w, 2921 w, 2855 w, 1638 s, 1596, 1569, 1554, 1518, 1477 s, 1444, 1393, 1360 w, 1320, 1308 s, 1283, 1256, 1202 w, 1180 w, 1156 w, 1124, 1090, 1075, 1045 w, 1028 w, 1000 w, 978, 927, 855, 824 w, 758, 723 s, 697, 619, 579, 443 w. Found, %: C 85.18; H 7.16; N 7.78. C$_{13}$H$_{13}$N. Calculated, %: C 85.21; H 7.15; N 7.84. The mother liquor was evaporated, and the residue was subjected to column chromatography on Al$_2$O$_3$ (diethyl ether–hexane, 1:3) to isolate 1.09 g (75%) of light yellow crystals containing (according to the ^{1}H and ^{13}C NMR data) 15% of 1-[(*Z*)-1-methyl-2-phenylvinyl]-1*H*-pyrrole and 85% of *E* isomer **VIII**.

Compounds **IX** and **X** were synthesized in a similar way.

1-[(*E*)-1-Methyl-2-(4-*tert*-butylphenyl)vinyl]-1*H*-pyrrole (IX). Yield 60%, light yellow crystals, mp 80°C (from hexane). IR spectrum, ν, cm^{-1}: 3139 w, 3100 w, 3053 w, 3024 w, 3000 w, 2962, 2901, 2866, 1723 w, 1686 w, 1639, 1607 w, 1551, 1517, 1480 s, 1458, 1445, 1412 w, 1395, 1368, 1358, 1313 s, 1296, 1284, 1270 w, 1257 w, 1202 w, 1191, 1119, 1089, 1074, 1042 w, 1025 w, 1013 w, 979, 928, 862, 836, 816, 725 s, 668, 637 w, 563, 516 w, 456 w. Found, %: C 85.28; H 8.79; N 5.83. C$_{17}$H$_{21}$N. Calculated, %: C 85.30; H 8.84; N 5.85.

1-[(*E*)-2-(4-Methoxyphenyl)-1-methylvinyl]-1*H*-pyrrole (X). Yield 60%, large light brown crystals, mp 101–102°C (from hexane). IR spectrum, ν, cm^{-1}: 3138 w, 3113 w, 3044 w, 3015 w, 2955 w, 2933 w, 2913 w, 2837 w, 1645, 1606, 1478, 1461, 1441, 1413 w, 1387, 1359 w, 1312 s, 1290 s, 1247 s, 1201 w, 1177, 1128, 1100, 1091, 1076, 1027, 977, 928, 852, 833, 817, 774 w, 731 s, 704 w, 668 w, 633 w, 616, 551,

530, 501 w, 450 w. Found, %: C 78.78; H 7.06; N 6.50. $C_{14}H_{16}NO$. Calculated, %: C 78.84; H 7.09; N 6.57.

1-[(*E*)-2-Methoxy-1-methylvinyl]-1*H*-pyrrole (XI) was synthesized as described above for compounds **VIII–X** from pyrrole and 3-methoxypropyne. Compound **XI** was formed as the minor product; according to the GLC data, its fraction in the reaction mixture was 25% (yield 14%). The major product was 1-(1-methoxymethylvinyl)-1*H*-pyrrole (66%); ^{1}H NMR spectrum, δ, ppm: 3.55 s (3H, OMe), 4.38 d (2H, CH$_2$), 4.95 m (1H, H$_A$), 6.15 t (2H, 3-H, 4-H), 6.57 d (1H, H$_B$), 6.68 t (2H, 2-H, 5-H); ^{13}C NMR spectrum, δ$_C$, ppm: 47.82 (OMe), 56.00 (CH$_2$), 98.94 (C$^\alpha$), 108.09 (C^3, C^4), 120.03 (C^2, C^5), 150.63 (C$^\beta$); also, the mixture contained 9% of unidentified products. Compound **XI** was isolated from the mixture as a light yellow liquid, n_D^{20} = 1.5155, purity 99%. IR spectrum, *v*, cm^{-1}: 3132 w, 3102 w, 3051 w, 2999, 2935, 2841, 2830, 1722, 1689, 1658, 1548 w, 1511 w, 1488 s, 1451, 1389 s, 1358 w, 1321 s, 1262, 1227 s, 1141 s, 1084, 1045, 1008, 970, 911, 840, 822, 725 s, 625, 505 w. Found, %: C 69.88; H 8.06; N 10.11. $C_8H_{11}NO$. Calculated, %: C 70.04; H 8.08; N 10.21.

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