

NMR Study of the Steric and Electronic Structure of 2-(2-Acylethenyl)pyrroles

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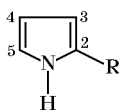
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Abstract—According to the ¹H and ¹³C NMR data, 2-(2-acylethenyl)- and 2-(2-acyl-1-phenylethenyl)pyrroles in chloroform exist exclusively in the keto form. The *Z* isomers of these compounds are characterized by coplanar arrangement of the olefinic fragment, carbonyl group, and pyrrole ring. The strong intramolecular hydrogen bond N–H···O is responsible for the presence of only one rotamer. The corresponding *E* isomers give rise to equilibrium between conformers with *syn* and *anti* arrangement of the olefinic fragment with respect to the pyrrole ring. A very strong conjugation between the ketovinyl group and the pyrrole ring is likely to arise from an appreciable contribution of the zwitterionic structure.

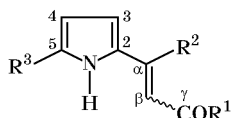
Reactions of pyrroles with acylacetylenes under certain conditions lead to the corresponding adducts, e.g., 2-(2-acylethenyl)- [1] and 2-(2-acyl-1-phenylethenyl)pyrroles [2]. Their molecules have a specific structure due to formation of a strong intramolecular hydrogen bond between the pyrrole NH hydrogen atom and oxygen atom of the carbonyl group in the *Z* isomers [1–4]. The N–H···O hydrogen bond and its effect on the structure of 2-(2-acyl-1-phenylethenyl)pyrroles were studied by IR spectroscopy [3], X-ray analysis [4], and quantum chemistry [4]. However, no detailed analysis of the ¹H and ¹³C NMR parameters have been performed so far, though it could provide an additional information on the steric and electronic structure of such compounds. In continuation of our

previous studies on intramolecular hydrogen bonding in various 2-substituted pyrroles [5, 6], in the present work we examined the ¹H and ¹³C NMR spectra of 2-(2-acylethenyl)pyrroles **IV–VIII** and 2-(2-acyl-1-phenylethenyl)pyrroles **IX–XIX**, as well as of model compounds **I–III** (Tables 1, 2).

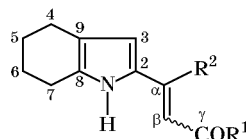
The assignment of signals in the ¹H and ¹³C NMR spectra of some compounds was a difficult task which was solved with the aid of homonuclear 2M ¹H–¹H spectroscopy (COSY [7] and NOESY [8]), as well as of heteronuclear 2M ¹H–¹³C HSQC [9] and HMBC [10] techniques. Signals from the quaternary carbon atoms C² and Cⁱ were assigned via correlation through three bonds with 4-H, 5-H, and *m*-H, respectively, in the HMBC spectrum.



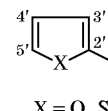
I–III



IV–VI, IX–XIV



VII, VIII, XV–XIX



X = O, S

I, R = H; **II**, R = COMe; **III**, R = COCF₃; **IV**, R¹ = Ph, R² = R³ = H; **V**, R¹ = 2-thienyl, R² = R³ = H; **VI**, R¹ = R³ = Ph, R² = H; **VII**, R¹ = Ph, R² = H; **VIII**, R¹ = 2-thienyl, R² = H; **IX**, R¹ = R² = Ph, R³ = H; **X**, R¹ = 2-furyl, R² = Ph, R³ = H; **XI**, R¹ = 2-thienyl, R² = Ph, R³ = H; **XII**, R¹ = Et, R² = R³ = Ph; **XIII**, R¹ = R² = R³ = Ph; **XIV**, R¹ = CCl₃, R² = R³ = Ph; **XV**, R¹ = R² = Ph; **XVI**, R¹ = 2-furyl, R² = Ph; **XVII**, R¹ = 2-thienyl, R² = Ph; **XVIII**, R¹ = Et, R² = Ph; **XIX**, R¹ = CCl₃, R² = Ph.

Table 1. ^1H NMR spectra of substituted pyrroles I–XIX

Comp. no.	Chemical shifts δ , ppm												$^3J_{\alpha,\beta}$, Hz
	H $^\alpha$	H $^\beta$	3-H	4-H	5-H	NH	<i>o</i> -H a (3'-H)	<i>m</i> -H a (4'-H)	<i>p</i> -H a (5'-H)	<i>o</i> -H b	<i>m</i> -H b	<i>p</i> -H b	
I			6.25	6.25	6.82	8.27							
II			6.93	6.28	7.07	9.28							
III			7.22	6.42	7.25	9.48							
IV	Z	6.93	6.65	6.65	6.35	7.08	13.10	7.98	7.47	7.52			12.3
	E	7.71	7.11	6.69	6.31	6.97	8.56	7.96	7.47	7.52			15.5
V	Z	6.88	6.52	6.63	6.30	7.05	12.72	7.75	7.12	7.60			12.2
	E	7.75	7.00	6.70	6.31	6.97	8.85	7.77	7.14	7.61			15.5
VI	Z	6.93	6.66	6.74	6.74		13.83	8.02	7.48	7.54	7.78 ^c	7.41 ^c	7.30 ^c
	E	7.77	7.17	6.78	6.64		8.93	7.98	7.49	7.51	7.55 ^c	7.39 ^c	7.29 ^c
VII^d	Z	6.80	6.42	6.40			12.88	8.02	7.48	7.54			12.2
	E	7.64	6.97	6.43			8.36	7.98	7.49	7.51			15.4
VIII^d	Z	6.75	6.38	6.38			12.72	7.71	7.10	7.56			12.0
	E	7.70	6.87	6.46			8.45	7.75	7.11	7.57			15.2
IX	Z		6.68	6.27	6.34	7.19	14.05	8.02	7.45	7.50	7.40	7.35	7.30
	E		7.19	6.61	6.33	6.92	8.30	7.90	7.46	7.49	7.40	7.35	7.30
X	Z		6.61	6.26	6.33	7.18	14.05	7.26	6.57	7.60	7.50	7.45	7.45
	E		7.16	6.60	6.30	6.88	8.29	7.08	6.46	7.50	7.38	7.38	7.27
XI	Z		6.56	6.21	6.30	7.14	13.90	7.75	7.10	7.60	f	f	f
XII^e	Z		6.02	6.27	6.68		14.43	7.81	7.48	7.32	f	f	f
XIII	Z		6.67	6.35	6.71		14.80	8.02	7.45	7.53	f	f	f
XIV	Z		6.53	6.50	6.77		13.74	7.78 ^c	7.47 ^c	7.32 ^c	f	f	f
XV^d	Z		6.47	5.98			13.88	7.94	7.35	7.45	f	f	f
XVI^d	Z		6.40	5.98			13.87	7.16	6.50	7.53	f	f	f
XVII^d	Z		6.39	5.95			13.71	7.68	7.07	7.54	f	f	f
XVIII^{d,e}	Z		5.83	5.91			13.47				f	f	f
XIX^d	Z		6.31	6.12			13.02				f	f	f

^a Signals from the γ -phenyl group.

^b Signals from the α -phenyl group.

^c Signals from the 5-phenyl group.

^d Signals from protons of the fused ring, δ , ppm: 1.75, 1.79 (5-H, 6-H); 2.50 (4-H); 2.65 (7-H).

^e Signals from protons of the γ -ethyl group, δ , ppm: **XII**: 2.70 (CH₂), 1.26 (CH₃); **XVIII**: 2.72 (CH₂), 1.24 (CH₃).

^f The *o*-H, *m*-H, and *p*-H protons give a broadened singlet at δ 7.45 ppm.

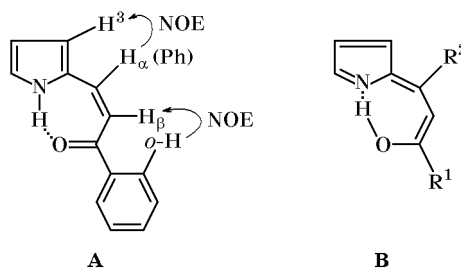
The NOESY spectrum of **VI** showed a correlation between 3-H of the pyrrole ring and H $^\alpha$ and between 4-H and *o*-H of the 5-phenyl ring, in keeping with the assignment made. Taking into account that the signal from *o*-H of the γ -phenyl group is displaced strongly downfield (σ 8.02 ppm), the other ^1H and ^{13}C signals of the above fragments can be assigned with certainty by the NOESY and HSQC techniques. The C^i resonance of the 5-phenyl group was identified through a cross peak with the 4-H signal in the HMBC spectrum.

The *o*-H signal from the α -phenyl group in pyrroles **IX**, **X**, and **XII–XIX** was assigned via correlation with the 3-H signal in the NOESY spectra. These data, in combination with the HSQC diagrams, made it possible to identify the other signals of that fragment. The C^α quaternary carbon atoms in molecules **IX**, **X**, and **XII–XIX** were assigned on the basis of a cross peak with 3-H in the HMBC spectrum.

Configurational isomers in the series of 2-(2-acyl-ethenyl)pyrroles **IV–VIII** were distinguished on the basis of the ^1H – ^1H vicinal coupling constant in the

olefinic fragment. It is equal to 12.0–12.3 Hz for the *Z* isomers and 15.2–15.5 Hz for the *E* isomer (Table 1). The unusually low (at first glance) difference in the $^3J_{\alpha,\beta}$ values of configurational isomers of pyrroles **IV–VIII** is typical of a ketovinyl fragment [11]. The *Z* and *E* isomers of 2-(2-acyl-1-phenylethenyl)pyrroles **IX–XIX** were distinguished on the basis of the 2M NOESY spectra which showed a correlation between signals from H^β and *o*-H of the phenyl ring in the *Z* isomers.

The most characteristic feature of the 1H NMR spectra of 2-(2-acylethenyl)- and 2-(2-acyl-1-phenylethenyl)pyrroles **IV–XIX** is a strong downfield shift of the NH signal in the *Z* isomers relative to its position in the spectra of the corresponding *E* isomers. The chemical shift of NH for the *Z* isomers of acylethenyl pyrrole derivatives **IV–VIII** ranges from 12.8 to 13.7 ppm, while the NH signal of analogous acyl-1-phenylethenylpyrroles **IX–XIX** is displaced even more downfield (up to 14.8 ppm). In the spectra of the *E* isomers of **IV–X**, the NH proton signal appears at δ 8.3–8.9 ppm (Table 1). Such a strong downfield shift of resonance proton signals provides a reliable support to participation of the respective proton in hydrogen bond formation (structure **A**).



In all previously studied 2-substituted pyrroles with intramolecular hydrogen bond, the $\delta(NH)$ value was smaller than 10 ppm. Even in the case of formation of a bifurcated bond, the NH chemical shift did not exceed δ 10.5 ppm [5]. For example, the $\delta(NH)$ values for 2-acetylpyrrole (**II**) and 2-trifluoroacetylpyrrole (**III**), which give rise to N–H...O intramolecular hydrogen bond [6], are equal to 9.28 and 9.48 ppm, respectively (Table 1). Moreover, the range of chemical shifts from 12 to 15 ppm is typical of hydroxy protons involved in intramolecular hydrogen bond [12]. These data prompted us to consider in more detail the possibility for transformation of the *Z* isomers of pyrrole derivatives **IV–XIX** into the enol form (structure **B**) while recording the NMR spectra. Keto–enol tautomerism in β -dicarbonyl compounds

Table 2. Parameters of the ^{13}C NMR spectra of compounds **I–IV**, **VI**, **VII**, **IX–XII**, and **XIV–XIX**

Compound no.	Chemical shifts δ_C , ppm							
	C^α	C^β	C^γ	C^2	C^3	C^4 (C^9)	C^5 (C^8)	
I				117.76	108.23	108.23	117.76	
II				132.27 (+14.5) ^a	116.96 (+8.7) ^a	110.68 (+2.5) ^a	124.87 (+7.1) ^a	
III				125.91 (+8.2) ^a	122.33 (+14.1) ^a	112.79 (+4.6) ^a	129.93 (+12.2) ^a	
IV	<i>Z</i>	135.58	111.68	190.79	130.66 (+12.9) ^a	120.57 (+12.3) ^a	111.74 (+3.5) ^a	123.80 (+6.0) ^a
	<i>E</i>	134.78	115.81	190.61	129.34 (+11.6) ^a	115.43 (+7.2) ^a	111.62 (+3.4) ^a	123.30 (+5.5) ^a
VI	<i>Z</i>	135.13	111.45	190.64	131.74 (+12.9) ^a	122.34 (+12.1) ^a	109.83 (+3.8) ^a	137.14 (+5.0) ^a
	<i>E</i>	134.46	115.61	190.50	130.45 (+11.6) ^a	117.14 (+6.9) ^a	109.58 (+3.6) ^a	137.50 (+5.4) ^a
VII	<i>Z</i>	135.31	109.11	190.06	129.67	120.08	122.50	136.05
	<i>E</i>	134.95	113.31	190.29	127.84	115.73	121.37	134.95
IX	<i>Z</i>	150.67	114.53	190.05	131.73 (+14.0) ^a	120.87 (+12.6) ^a	111.45 (+3.2) ^a	123.85 (+6.1) ^a
	<i>E</i>	147.32	115.60	190.60	132.64 (+14.9) ^a	112.42 (+4.2) ^a	111.20 (+3.0) ^a	122.14 (+4.4) ^a
X	<i>Z</i>	150.77	113.17	177.52	131.75	120.85	111.49	124.18
XI	<i>Z</i>	150.27	113.66	181.82	131.62	120.85	111.37	124.12
XII^b	<i>Z</i>	148.34	116.84	201.28	132.28	121.59	108.98	136.76
XIV^b	<i>Z</i>	154.57	106.52	180.87	132.30	125.83	110.73	140.26
XV^b	<i>Z</i>	150.39	112.09	189.00	130.52	120.30	122.48	136.22
XVI^b	<i>Z</i>	150.45	110.67	176.58	130.54	120.25	122.69	136.63
XVII^b	<i>Z</i>	149.98	111.18	180.88	130.44	120.32	122.38	136.58
XVIII^b	<i>Z</i>	148.40	114.99	200.48	130.04	119.17	121.58	134.96
XIX^b	<i>Z</i>	154.55	104.14	180.11	130.53	123.49	124.07	140.18

Table 2. (Contd.)

Compound no.	Chemical shifts δ_C , ppm								
	C^i (C^2) ^c	C^o (C^3) ^c	C^m (C^4) ^c	C^p (C^5) ^c	$C^{i d}$	$C^{o d}$	$C^{m d}$	$C^{p d}$	
IV	Z	139.77	128.27	128.64	132.40				
	E	138.71	128.35	128.63	132.49				
VI	Z	140.13	128.27	128.63	132.26	131.48 ^e	124.85 ^e	129.12 ^e	127.84 ^e
	E	138.91	128.40	128.62	132.45	131.45 ^e	124.67 ^e	129.16 ^e	127.71 ^e
VII	Z	140.35	128.24	128.52	132.11				
	E	139.16	128.06	128.52	131.90				
IX	Z	140.45	128.35	128.59	132.27	143.28	128.03	129.16	128.51
	E	139.36	128.40	128.40	132.27	137.70	128.40	129.13	128.54
X	Z	155.06	116.87	112.68	146.21	142.99	128.03	129.13	128.53
XI	Z	147.62	131.23	128.38	133.44	142.97	128.02	129.09	128.51
XII ^b	Z	131.71 ^e	124.71 ^e	129.12 ^e	127.64 ^e	142.56	128.02	129.12	128.42
XIV ^b	Z	130.70 ^e	125.24 ^e	129.32 ^e	129.23 ^e	142.12	128.23	129.22	128.78
XV ^b	Z	141.06	128.10	129.10	131.77	143.49	127.80	128.50	128.22
XVI ^b	Z	155.30	115.86	112.50	145.77	143.23	127.89	129.08	128.23
XVII ^b	Z	148.22	130.40	128.22	132.60	143.30	127.92	129.10	128.22
XVIII ^b	Z					143.16	127.81	129.03	128.05
XIX ^b	Z					142.59	128.04	128.89	128.89

^a In parentheses is given the difference in the chemical shift relative to pyrrole.

^b Other signals, δ_C , ppm: **XII**: 38.01, 9.82 (CH_2CH_3); **XVIII**: 37.57, 9.55 (CH_2CH_3); **XIV**: 98.32 (CCl_3); **XIX**: 98.60 (CCl_3); *E-VII*: 22.77 (C^4), 23.22 (C^5), 22.99 (C^6), 23.49 (C^7); *Z-VII*: 22.77 (C^4), 23.20 (C^5), 23.00 (C^6), 23.72 (C^7); **XV**: 22.93 (C^4), 23.61 (C^5), 23.05 (C^6), 23.79 (C^7); **XVI**: 22.92 (C^4), 23.60 (C^5), 23.04 (C^6), 23.80 (C^7); **XVII**: 22.90 (C^4), 23.62 (C^5), 23.05 (C^6), 23.82 (C^7); **XVIII**: 22.88 (C^4), 23.66 (C^5), 23.12 (C^6), 23.66 (C^7); **XIX**: 22.82 (C^4), 23.37 (C^5), 22.82 (C^6), 23.96 (C^7).

^c Signals from the γ -phenyl group.

^d Signals from the α -phenyl group.

^e Signals from the 5-phenyl groups.

was thoroughly studied by NMR spectroscopy several decades ago [13–18], and studies in this field are performed at present [19, 20]. The transformation of a compound from ketone to enol form is accompanied by sharp variation of its ^1H and ^{13}C NMR parameters [13–18]. Identification of tautomers by comparison of the spectral parameters of the *Z* and *E* isomers of **IV–X** could lead to misinterpretation, for the *E* isomer can also exist in the enol form [15].

The chemical shifts of C^i in the *Z* and *E* isomers of 2-(2-benzoylphenyl)pyrrole (**IV**) almost coincide with that of the corresponding *N*-vinyl derivative which is known to exist in the keto form (δ_C 189.82 ppm [21]). The enol form should be characterized by an appreciably downfield shift of that signal [22]. In going to the enol form, the endocyclic pyrrole nitrogen atom becomes pyridine-like. By considering ^{13}C chemical shifts of a large series of azoles [23] and comparing the chemical shifts of pyrrole and pyridine [24] we come to a conclusion that in the spectrum of the enol form the C^5 signal should be displaced strongly down-

field. In fact, a downfield shift of the signal from C^5 (by 5–6 ppm) relative to that of unsubstituted pyrrole is observed for compounds **IV**, **VI**, and **IX**; however, even greater shift (more than 12 ppm; Table 2) was detected for the C^3 signal. An analogous shift of the C^5 resonance is typical of 2-acetylpyrrole (**II**) which exists exclusively in the keto form [25], whereas for 2-trifluoroacetylpyrrole (**III**) it is much greater. Therefore, the effect of 2-substitution in the heteroring on the chemical shift of C^5 in the ^{13}C NMR spectra of pyrroles **IV**, **VI**, and **IX** should be explained exceptionally in terms of electronic influence of the ketovinyl group rather than by occurrence of tautomeric equilibria.

According to the data of [15, 19], proton coupling constants are very sensitive to keto–enol transformations. However, the ^1H – ^1H coupling constants both in the ketovinyl fragment (compounds **IV–VIII**; Table 1) and in the pyrrole ring ($^3J_{3,4} = 3.7$, $^3J_{4,5} = 2.5$; $^4J_{3,5} = 1.2$ Hz) of compounds **I–VI** and **IX–XIV** remain essentially the same. Furthermore, in the

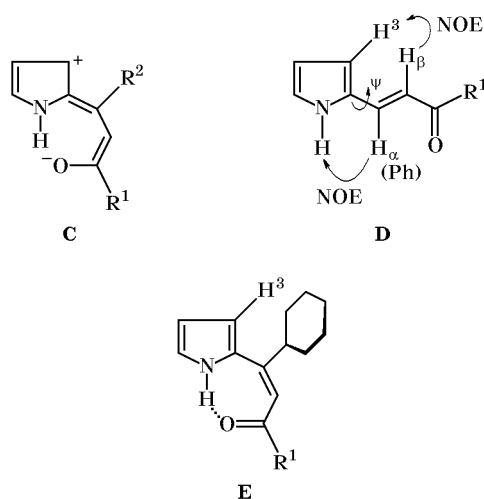
spectra of **IV–XIX** we observed coupling constants between the pyrrole ring protons and proton of the NH group ($^4J_{\text{NH},3\text{-H}} = 2.4$, $^4J_{\text{NH},4\text{-H}} = 2.1$, $^3J_{\text{NH},5\text{-H}} = 1.8$ Hz). The above spectral data led us to conclude that 2-(2-acylethenyl)- and 2-(2-acyl-1-phenylethenyl)-pyrroles **IV–XIX** in chloroform exist exclusively in the keto form. According to the X-ray diffraction data, the keto tautomer is typical of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (**XIII**) in crystal [4]. Therefore, a very large downfield shift of the NH signal in the spectra of the *Z* isomers of **IV–XIX** results from much greater strength of the intramolecular hydrogen bond N–H \cdots O, as compared to 2-(2-pyridyl)pyrrole where N–H \cdots N intramolecular hydrogen bond is formed [5] or 2-acetyl- and trifluoroacetylpyrroles **II** and **III**. This conclusion is supported by the IR spectral data. The low-frequency shift of the N–H stretching vibration band in the IR spectra of 2-(2-pyridyl)pyrrole and pyrroles **II** and **III** is only several tens cm^{-1} (ν_{NH} 3458 and 3446 cm^{-1} for compounds **II** and **III**, respectively; see also [5, 6]), while the corresponding shift for the *Z* isomers of **IV–XIX** reaches 300–400 cm^{-1} and is accompanied by very strong broadening of the absorption band [3]. Presumably, such strong differences in the spectral patterns conform to two different kinds of H-bonding: electrostatic, which is likely to occur in 2-(2-pyridyl)pyrrole and compounds **II** and **III**, and covalent, which is observed for the *Z* isomers of pyrroles **IV–XIX** [26, 27].

The data in Table 2 show that introduction of a phenyl ring into position 1 of the ketovinyl fragment leads to a regular downfield shift of the NH signal (by about 1 ppm; cf. compounds **IV–VIII** and **IX**, **XI**, **XIII**, **XV**, and **XVII**). The same effect was observed previously for β -dicarbonyl compounds existing in the enol form with O–H \cdots O intramolecular hydrogen bond [13, 16]. It is explained by mutual repulsion of unsaturated groups, which causes contraction of H-chelate ring and strengthening of the hydrogen bond due to shortening of the distance between the heteroatoms [13, 16]. Just the latter factor (shortening of the distance between the nitrogen atom and carbonyl oxygen atom) is responsible for enhancement of hydrogen bonding in 2-(2-acyl-1-phenylethenyl)-pyrroles **IX–XIX** relative to 2-(2-acylethenyl)pyrroles **IV–VIII**.

Molecules **IV–XIX** possess several unsaturated fragments capable of participating in π,π -interactions which is determined by their steric structure. The character of such interactions may be estimated on the basis of the ^{13}C chemical shifts. The $\text{C}^\alpha=\text{C}^\beta$ bond in

pyrroles **IV–XIX** is strongly polarized, for it is located between a π -donor (pyrrole ring) and π -acceptor (carbonyl group) fragments. The difference between δ_{C^α} and δ_{C^β} in the *Z* isomers of **IV–XIX** is 24–26 ppm, and it decreases to 19–21 ppm in going to the *E* isomers. Acceptor effect of the entire ketovinyl group leads to downfield shift of signals from all carbon atoms of the pyrrole ring (Table 2).

On the other hand, the data in Table 2 show that the ketovinyl fragment in the *Z* and *E* isomers of pyrroles **IV** and **VI** differently affects ^{13}C chemical shifts of the pyrrole ring. The shifts of the C^4 and C^5 signals are almost similar for both isomers, whereas the C^3 signal of the *Z* is displaced appreciably more strongly than the C^3 signal of the *E* isomer ($\Delta\delta_{\text{C}^3}$ 12 and 7 ppm, respectively). Taking into account that the intramolecular hydrogen bond N–H \cdots O in the *Z* isomer is stronger, it is reasonable to presume that its structure is planar, which ensures very effective π,π -interaction between the ketovinyl group and the pyrrole ring. The planar arrangement of the double $\text{C}^\alpha=\text{C}^\beta$ bond and pyrrole ring in molecule **XIII** in crystal was proved by X-ray analysis [4]. Much greater displacement of the C^3 signal in the spectra of pyrroles **IV–VI** due to electronic effect of the ketovinyl fragment (as compared to C^4 and C^5) suggests much more effective conjugation of the $\text{C}=\text{C}-\text{C}(\text{O})\text{Ph}$ group with the pyrrole C^2-C^3 bond than with C^4-C^5 . This may be interpreted in terms of some contribution of zwitterionic structure **C** to the ground state of the molecule.



Intramolecular hydrogen bond in the *E* isomers of **IV–VI** does not fix their planar structure, so that the $\text{C}^\alpha=\text{C}^\beta$ bond plane and the pyrrole ring can form a dihedral angle Ψ and a rotamer with *trans* arrangement of these fragments (structure **D**) could appear as

well. As a result, the contribution of the zwitterionic structure into the ground state of molecules **IV–VI** is reduced, and π -polarization of the $C^\alpha=C^\beta$ decreases, leading to downfield shift of the C^β and β -H signals by 4 and 0.5 ppm, respectively, in going from the *Z* to *E* isomer.

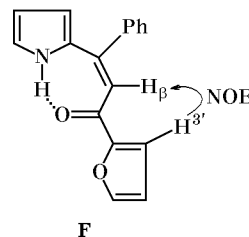
Coplanar arrangement of the $C^\alpha=C^\beta$ band and pyrrole ring in the *Z* isomer of 2-(2-benzoyl-1-phenylethenyl)pyrrole (**IX**) should cause sharp deviation of the phenyl ring from the above planes. The observed upfield shift of the 3-H signal in the spectrum of *Z-IX* as compared to *Z-IV* ($\Delta\delta$ 0.4 ppm) is induced by the ring current effect of the phenyl group. It follows that the 3-H proton is located above the phenyl ring as shown in structure **E** and hence the phenyl ring in **IX** is actually forced out from the pyrrole ring (double bond) plane. The corresponding dihedral angle in molecule **XIII** in crystal is equal to 54° [4]. In the ^1H NMR spectrum of *E-IX*, a strong upfield shift is observed for the NH signal (Table 1). This means that the predominant tautomer is characterized by *trans* arrangement of the ketovinyl group and pyrrole ring. It should be noted that the downfield shift of the C^3 signal in the ^{13}C NMR spectrum of phenyl-substituted pyrrole **IX**, which is induced by conjugation between the pyrrole ring and ketovinyl fragment, is as small as 4 ppm against 7 ppm for pyrroles **IV** and **VI** (Table 2). Unfavorable conditions for conjugation between the pyrrole ring and ketovinyl fragment in **IX** may be explained by increase of the angle Ψ owing to steric effect of the α -phenyl ring (structure **D**).

The formation of a common π -conjugated system involving the pyrrole ring and ketovinyl group in molecules **IV–XIX** ensures a good transmission of electronic effects of the substituent in the ketovinyl group to the heteroring. For example, in going from ethyl group to trichloromethyl (pyrroles **XII** and **XIV**; tetrahydroindoles **XVIII** and **XIX**), the C^3 and C^5 (C^8) signals shift downfield by 3.5–5.0 ppm. Moreover, the signal from the *para*-carbon atom of the 5-phenyl ring in **XIV** shifts downfield ($\Delta\delta$ 1.6 ppm), indicating that the effect of the CCl_3 group is transmitted through the ketovinyl fragment and the pyrrole ring. On the other hand, we observed no effect of the same substituent on the phenyl group located in the α -position of the ethenyl group: the chemical shifts of the corresponding *para*-carbon atoms in molecules **XII**, **XIV** and **XVIII**, **XIX** differ insignificantly. The reason is that the α -phenyl ring is not involved in conjugation, for it is turned through some angle relative to the plane formed by the $C^\alpha=C^\beta$ double bond and the heteroring.

An additional information on the steric structure of the compounds under study can be obtained by analyzing nuclear Overhauser effects (NOE) using 2M NOESY diagram. The *Z* isomer of **IV** showed in the NOESY spectrum cross peaks between α -H and 3-H and between β -H and *o*-H. Therefore, the $C^\alpha=C^\beta$ bond is located *syn* with respect to the pyrrole nitrogen atom and is oriented *trans* relative to the phenyl ring (see structure **A**). Just that arrangement of the unsaturated fragments corresponds to the structure of the *Z* isomer of **IV**, stabilized by the intramolecular hydrogen bond $\text{N-H}\cdots\text{O}$. In the NOESY spectrum of *E-IV*, correlation was observed between the 3-H proton, on the one hand, and both α -H and β -H, on the other. In addition, the latter protons displayed an off-diagonal peak with NH. These data must be interpreted as equilibrium between stereoisomers with *syn* and *anti* arrangement of the $C^\alpha=C^\beta$ bond with respect to the pyrrole nitrogen atom (see structure **D**). Cross peak between β -H and *o*-H is retained. Therefore, *trans* orientation of the $C^\alpha=C^\beta$ bond relative to the phenyl group remains unchanged in going from the *Z* to *E* isomer of **IV**. In the latter, the α -H proton appears spatially close to the carbonyl oxygen atom (structure **D**), and the chemical shift of α -H increases by 0.8 ppm relative to that in the *Z* isomer (Table 1).

The presence of cross peaks between 3-H and *o*-H (in the α -phenyl group), as well as for β -H and *o*-H (in the γ -phenyl group), in the NOESY spectrum of *Z-IX* is consistent with the assigned structure which is analogous to *Z-IV*. The NOESY spectrum of the *E* isomer of **IX** is characterized by correlation of 3-H with α -H and β -H, indicating the existence of rotamers with *syn* and *anti* arrangement of the $C^\alpha=C^\beta$ bond relative to the pyrrole nitrogen atom.

Finally, the *E* and *Z* isomers of compound **X** showed in the NOESY spectrum intense cross peaks for β -H and 3'-H (in addition to those typical of **IX**). This means a considerable contribution of a conformation in which the furyl group is oriented *syn* with respect to the carbonyl group (structure **F**).



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