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# $^1$H and $^{13}$C NMR Study of Steric and Electronic Structure of 2-(2-Acylethenyl)-1-vinylpyrroles*

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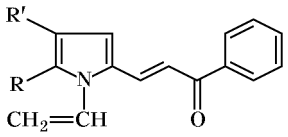
**Abstract**—According to the $^1$H and $^{13}$C NMR data, the molecule of 2-(2-benzoylethenyl)-1-vinylpyrrole has a nearly planar structure with *trans* arrangement of the vinyl and oxovinyl groups. The unsaturated fragments give rise to effective conjugation. The vinyl group in 5-substituted 2-(2-acylethenyl)-1-vinylpyrroles strongly deviates from the heteroring plane because of steric effect of the substituent; however, this effect does not change the arrangement of the other unsaturated fragments.

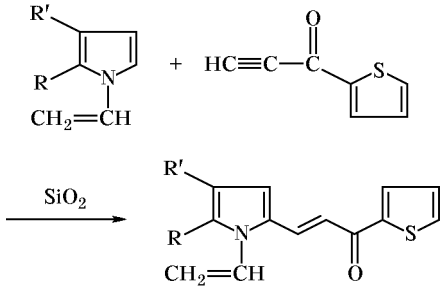
$^1$H and $^{13}$C NMR studies of a wide series of substituted 1-vinylpyrroles revealed relations between the shielding constants of the β-proton and β-carbon atom in the vinyl group, as well as direct ($^1J_{C,H}$) and long-range coupling constants ($J_{H,H}$) through 4, 5, and 6 bonds and internal rotation potential [1–4]. The spectral relations thus obtained were used in the conformational analysis of recently synthesized 2-(2-acylethenyl)-1-vinylpyrroles. 2-(2-Benzoylethenyl)-1-vinylpyrroles **I**–**VIII** were prepared from the corresponding 1-vinylpyrroles and benzoylacetylene by the procedure reported in [5].



**I**–**VIII**

**I**, R = R′ = H; **II**, R = Me, R′ = H; **III**, RR′ = $(CH_2)_4$; **IV**, R = Ph, R′ = H; **V**, R = Me, R′ = Pr; **VI**, R = Ph, R′ = Et; **VII**, R = Bu, R′ = Pr; **VIII**, R = 2,5-$Me_2C_6H_3$, R′ = H.

2-(2-Thenoylethenyl)-1-vinyl-4,5,6,7-tetrahydroindole (**IX**) and 2-(2-thenoylethenyl)-1-vinyl-5-phenylpyrrole (**X**) were synthesized by solid-phase C-vinylation of 1-vinyl-4,5,6,7-tetrahydroindole and 5-phenyl-1-vinylpyrrole, respectively, with thenoylacetylene over silica gel surface without a solvent:



**IX**, **X**

**IX**, RR′ = $(CH_2)_4$; **X**, R = Ph, R′ = H.

Examination of the conjugation-induced signal shifts in the NMR spectra requires reliable assignment of these signals to be done. Signal assignment in the spectra of 2-(2-acylethenyl)-1-vinylpyrroles **I**–**X** is a complex problem which could be solved with the aid of two-dimensional NMR techniques. The $^1$H and $^{13}$C NMR parameters of substituted pyrroles **I**–**X** are collected in Tables 1 and 2. The $^1$H NMR signals were assigned by analysis of the $^1$H–$^1$H NOESY [6] and COSY spectra [7]. The NOESY spectra of all compounds **I**–**X** contain a cross-peak between the β′-H proton and $H_X$ proton of the 1-vinyl group,

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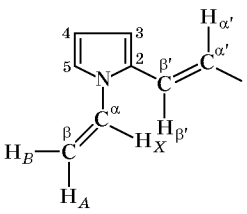
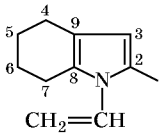
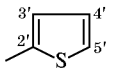
**Table 1.** $^1$H NMR spectra of 2-(2-acylethenyl)-1-vinylpyrroles **I**–**X** and 1-vinylpyrrole (**XI**)[a]







| Compound no. | Chemical shifts δ, ppm | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 3-H | 4-H | 5-H | $H_X$ | $H_A$ | $H_B$ | δ[b] | α′-H | β′-H |
| **I** | 6.84 | 6.31 | 7.14 | 7.14 | 4.95 | 5.25 | 0.30 | 7.31 | 7.82 |
| **II** | 6.79 | 6.03 | – | 6.81 | 5.38 | 5.21 | –0.17 | 7.24 | 7.80 |
| **III** | 6.68 | – | – | 6.84 | 5.22 | 5.14 | –0.06 | 7.22 | 7.83 |
| **IV** | 6.97 | 6.4 | – | 6.83 | 5.37 | 5.19 | –0.18 | 7.38 | 7.94 |
| **V** | 6.75 | – | – | 6.82 | 5.36 | 5.19 | –0.17 | 7.25 | 7.84 |
| **VI** | 6.90 | – | – | 6.67 | 5.15 | 5.00 | –0.15 | 7.32 | 7.93 |
| **VII** | 6.74 | – | – | 6.79 | 5.37 | 5.19 | –0.18 | 7.22 | 7.82 |
| **VIII** | 6.94 | 6.21 | – | 6.67 | 5.04 | 4.93 | –0.11 | 7.35 | 7.93 |
| **IX** | 6.68 | – | – | 6.84 | 5.22 | 5.14 | –0.08 | 7.10 | 7.84 |
| **X** | 6.98 | 6.42 | – | 6.85 | 5.38 | 5.20 | –0.18 | 7.24 | 7.95 |
| **XI** [1] | 6.23 | 6.23 | 6.88 | 6.81 | 4.63 | 5.08 | 0.45 | – | – |

[a] Other signals, δ, ppm: **II**: 2.27 (5-Me); **III**: 2.61 (7-H), 2.52 (4-H), 1.76 (5-H, 6-H); **IV**; 7.45 (*o*-H), 7.35 (*p*-H), 7.40 (*m*-H) (5-Ph); **V**: 2.21 (5-Me), 2.38 (1-$CH_2$), 1.57 (2-$CH_2$), 0.96 ($CH_3$) (4-Pr); **VI**: 7.40 (*o*-H), 7.35 (*p*-H, *m*-H) (5-Ph), 2.42 ($CH_2$), 1.14 ($CH_3$) (4-Et); **VII**: 2.56 (1-$CH_2$), 1.43 (2-$CH_2$), 1.33 (3-$CH_2$), 0.90 ($CH_3$) (5-Bu), 2.35 (1-$CH_2$), 1.57 (2-$CH_2$), 0.95 ($CH_3$) (4-Pr); **VIII**: 7.11, 7.04, 7.00 (ring protons), 2.33, 2.10 ($CH_3$ in the 5-substituent); **IX**: 7.59 (5′-H), 7.13 (4′-H), 7.75 (3′-H), 2.60 (7-H), 2.52 (4-H), 1.76 (5-H, 6-H); **X**: 7.63 (5′-H), 7.16 (4′-H), 7.82 (3′-H), 7.46 (*o*-H), 7.35 (*p*-H), 7.39 (*m*-H) (5-Ph). Signals from protons of the phenyl ring at the ketovinyl group are located in the δ regions 7.95–8.00 (*o*-H) and 7.30–7.50 ppm (*m*-H, *p*-H).

[b] $\delta = \delta(H_B) - \delta(H_A)$.

which allows us to identify the signal of the former. The α′-H proton gives cross-peaks with the *ortho*-protons (*o*-H) of the benzoylethenyl group in 2-(2-benzoylethenyl)-1-vinylpyrroles **I**–**VIII** or with 3′-H of the thiophene ring in 2-(2-thenoylethenyl)-1-vinylpyrroles **IX** and **X**. The $^1$H NMR signals from the alkyl substituents in **VII** and **VIII** were assigned on the basis of the COSY spectra. The $^{13}$C signals of carbon atoms attached to hydrogen were identified using heteronuclear $^1$H–$^{13}$C HSQC technique [8]. The signals from quaternary carbon atoms were determined by analysis of the heteronuclear $^1$H–$^{13}$C HMBC spectra [9]. For example, the presence of cross-peaks between the 5-H and 4-H signals and the $^{13}$C signal at $\delta_C$ 129.99 ppm in the HMBC spectrum of 2-(2-benzoylethenyl)-1-vinylpyrrole (**I**) indicates that the latter belongs to $C^2$ in the ring. The aromatic carbon signals of compounds **IV** and **VI** were discriminated by comparison of carbon chemical shifts of the phenyl ring attached to the carbonyl group with the corresponding chemical shifts of compounds **I**–**III** and **VI**–**VIII**, as well as by analysis of unidimensional cross-sections of the HSQC spectra.

Comparison of the $^{13}$C NMR chemical shifts in the spectra of compounds **I**–**X** provides information on conjugation between unsaturated fragments in their molecules. The oxovinyl group exerts a considerable effect on the positions of signals from the pyrrole ring and 1-vinyl group. This follows from the chemical shifts of 2-(2-benzoylethenyl)-1-vinylpyrrole (**I**) and 1-vinylpyrrole (**XI**). The presence of oxovinyl group in the former induces downfield shifts of the $C^3$, $C^5$, and $C^\beta$ signals by 3.2, 4.2, and 6.3 ppm, respectively. This is the result of effective π,π-interaction where the benzoylvinyl fragment acts as acceptor. π,π-Conjugation is possible in the case of nearly coplanar arrangement of the interacting fragments. In the series of 2-(2-acylethenyl)-1-vinylpyrroles **IV**, **VIII**, and **X**, the chemical shift of $C^2$ increases, respectively, by 1.4, 0.8, and 1.26 ppm relative to the chemical shift of

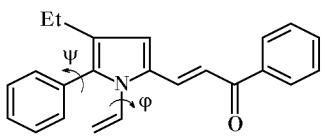
**Table 2.** $^{13}$C NMR spectra of 2-(2-acylethenyl)-1-vinylpyrroles **I**–**X** and 1-vinylpyrrole (**XI**)[a]

| Compound no. | Chemical shifts $\delta_C$, ppm | | | | | | |
|---|---|---|---|---|---|---|---|
| | $C^2$ | $C^3$ | $C^{4(9)}$ | $C^{5(8)}$ | $C^{\alpha}$ | $C^{\beta}$ | $C^{\alpha'}$ |
| **I** | 129.99 | 113.36 | 111.75 | 122.87 | 130.25 | 103.17 | 118.38 |
| **II** | 129.89 | 113.21 | 110.54 | 135.22 | 130.18 | 113.93 | 116.07 |
| **III** | 129.02 | 112.67 | 121.52 | 135.04 | 129.73 | 110.74 | 115.76 |
| **IV** | 131.39 | 113.20 | 111.87 | 138.77 | 130.95 | 114.60 | 117.53 |
| **VI** | 129.66 | 112.85 | 127.41 | 135.54 | 130.74 | 112.71 | 117.12 |
| **VII** | 128.64 | 113.46 | 124.04 | 136.74 | 130.27 | 114.43 | 115.40 |
| **VIII** | 130.84 | 113.14 | 112.20 | 138.45 | 130.16 | 111.66 | 117.28 |
| **IX** | 128.79 | 112.68 | 121.53 | 135.15 | 129.65 | 110.76 | 115.40 |
| **X** | 131.25 | 113.28 | 111.90 | 138.84 | 130.95 | 114.63 | 117.34 |
| **XI** [1] | 118.67 | 110.15 | 110.15 | 118.67 | 133.04 | 96.83 | – |

| Compound no. | Chemical shifts $\delta_C$, ppm | | | | | |
|---|---|---|---|---|---|---|
| | $C^{\beta'}$ | C=O | $C^{i(2')}$ | $C^{o(3')}$ | $C^{m(4')}$ | $C^{p(5')}$ |
| **I** | 131.69 | 189.82 | 138.58 | 128.37 | 1228.66 | 132.63 |
| **II** | 133.66 | 190.04 | 138.91 | 128.225 | 128.56 | 132.30 |
| **III** | 133.32 | 189.82 | 139.10 | 128.24 | 128.53 | 132.30 |
| **IV** | 133.67 | 189.94 | 138.76 | 128.33 | 128.61 | 133.67 |
| **VI** | 133.64 | 189.90 | 138.95 | 128.33 | 128.58 | 132.36 |
| **VII** | 133.85 | 190.00 | 139.21 | 128.24 | 128.51 | 132.13 |
| **VIII** | 133.75 | 190.10 | 138.88 | 128.33 | 128.61 | 132.42 |
| **IX** | 132.50 | 181.77 | 146.45 | 130.65 | 128.09 | 132.76 |
| **X** | 132.91 | 181.73 | 146.21 | 131.05 | 128.21 | 133.18 |
| **XI** [1] | – | – | – | – | – | – |

[a] Other signals, $\delta_C$, ppm: **II**: 13.63 (5-Me); **III**: 22.96 ($C^4$), 23.13 ($C^5$, $C^6$), 23.81 ($C^7$); **IV**: 132.09 ($C^i$), 128.52 ($C^o$), 128.90 ($C^m$), 127.81 ($C^p$) (5-Ph); **VI**: 130.54 ($C^o$), 128.40 ($C^m$), 128.40 ($C^p$), 131.61 ($C^i$) (5-Ph), 19.22 ($CH_2$), 15.41 ($CH_3$) (4-Et); **VII**: 24.73 (1-$CH_2$), 31.77 (2-$CH_2$), 22.68 (3-$CH_2$), 13.94 ($CH_3$) (5-Bu), 28.02 (1-$CH_2$), 24.08 (2-$CH_2$), 14.21 ($CH_3$) (4-Pr); **VIII**: 21.23, 20.07 (Me), 130.80, 130.16, 131.48 (CH in the 5-substituent); **IX**: 22.93 ($C^4$), 23.09 ($C^5$, $C^6$), 23.77 ($C^7$); **X**: 132.12 ($C^i$), 128.93 ($C^o$), 128.53 ($C^m$), 127.83 ($C^p$) (5-Ph).

$C^2$ in pyrrole **I** due to electronic effect of the phenyl substituent. The chemical shift of $C^{\beta}$ in the 1-vinyl group varies over the widest range. The strongest change in the position of the $C^{\beta}$ signal is observed on introduction of a substituent into position *5* of the pyrrole ring. The downfield of the $C^{\beta}$ signal by 10.8 ppm in the spectrum of 2-(2-benzoylethenyl)-5-methyl-1-vinylpyrrole (**II**), as compared to pyrrole **I**, is caused by displacement of electron density on the double bond in the 1-vinyl group from the β-position to the ring. This corresponds to weakening of *p*,π-conjugation between the above fragments as a result of distortion of planar structure of the molecule [1]. Such steric effect of the R substituent on *p*,π-conjugation with the 1-vinyl group is typical of all the examined 2-(2-acylethenyl)-1-vinylpyrroles **I**–**X**. Comparison of the $^{13}$C NMR spectra of compounds **IV** and **VI** shows the effect of the alkyl substituent R′ on electron density distribution in the conjugated π-systems. Introduction of an ethyl group into position *4* of the pyrrole ring leads to shielding of $C^2$, $C^3$, $C^5$, and $C^{\beta}$ by 1.7, 0.35, 3.2, and 1.9 ppm, respectively. Apart from the purely electronic effect of the 4-ethyl group, the above shifts originate from weakening of π,π-conjugation between the benzene and pyrrole rings due to distortion of their coplanarity (increase of the




**A**

**Table 3.** Coupling constants in the NMR spectra of 2-(2-acylethenyl)-1-vinylpyrroles **I**–**X** and 1-vinylpyrrole (**XI**)[a]

| Compound no. | Coupling constants *J*, Hz | | | | |
|---|---|---|---|---|---|
| | $^2J(H_A, H_B)$ | $^3J(H_A, H_X)$ | $^3J(H_B, H_X)$ | $^3J(\alpha'\text{-H}, \beta'\text{-H})$ | $^1J(C^{\alpha}, H_X)$ |
| **I** | –1.25 | 8.8 | 15.5 | 15.3 | 176.5 |
| **II** | –0.70 | 8.5 | 15.7 | 15.3 | 177.2 |
| **III** | –0.75 | 8.7 | 15.8 | 15.2 | 176.3 |
| **IV** | –0.80 | 8.4 | 15.7 | 15.3 | 177.1 |
| **V** | –0.75 | 8.5 | 15.7 | 15.3 | – |
| **VI** | –0.75 | 8.5 | 15.7 | 15.2 | 177.3 |
| **VII** | –0.75 | 8.4 | 15.7 | 15.3 | 176.9 |
| **VIII** | –0.75 | 8.5 | 15.7 | 15.2 | 177.3 |
| **IX** | –0.75 | 8.4 | 15.7 | 15.2 | 177.6 |
| **X** | –0.75 | 8.4 | 15.7 | 15.2 | 176.1 |
| **XI** [1] | –1.2 | 8.9 | 15.9 | – | 174.2 |

| Compound no. | Coupling constants *J*, Hz | | | | |
|---|---|---|---|---|---|
| | $^1J(C^{\beta}, H_A)$ | $^1J(C^{\beta}, H_B)$ | $\Delta J$ | $^1J(C^{\alpha'}, \alpha'\text{-H})$ | $^1J(C^{\beta'}, \beta'\text{-H})$ |
| **I** | 164.3 | 157.8 | 6.5 | 157.0 | 153.5 |
| **II** | 162.1 | 159.3 | 2.8 | 157.0 | 153.5 |
| **III** | 162.1 | 159.3 | 2.8 | 157.3 | 153.5 |
| **IV** | _[b] | _[b] | _[b] | 157.4 | 154.1 |
| **V** | – | – | – | – | – |
| **VI** | 162.7 | 159.5 | 3.2 | 156.6 | 155.2 |
| **VII** | 161.7 | 159.2 | 2.5 | 156.4 | 154.2 |
| **VIII** | 162.2 | 159.5 | 2.7 | 156.7 | 154.6 |
| **IX** | 162.0 | 159.0 | 3.0 | 157.2 | 153.7 |
| **X** | _[b] | _[b] | _[b] | 157.4 | 155.1 |
| **XI** [1] | 164.0 | 157.0 | 7.0 | – | – |

[a] Other coupling constants, *J*, Hz: **I**: 0.40 $^4J(5\text{-H}, H_X)$, 0.60 $^5J(4\text{-H}, H_X)$, 0.40 $^6J(5\text{-H}, H_A)$, 0.40 $^4J(3\text{-H}, \beta'\text{-H})$, 0.60 $^5J(4\text{-H}, \beta'\text{-H})$, 171.2 $^1J(C^3, 3\text{-H})$, 174.0 $^1J(C^4, 4\text{-H})$,185.9 $^1J(C^5, 5\text{-H})$; $^5J(4\text{-H}, \beta'\text{-H})$, 171.4 $^1J(C^3, 3\text{-H})$, 172.0 $^1J(C^4, 4\text{-H})$; **III**: 169.8 $^1J(C^3, 3\text{-H})$; **IV**: 0.60 $^5J(4\text{-H}, \beta'\text{-H})$, 172.5 $^1J(C^3, 3\text{-H})$, 171.7 $^1J(C^4, 4\text{-H})$; **VI**: 168.7 $^1J(C^3, 3\text{-H})$; **VII**: 168.4 $^1J(C^3, 3\text{-H})$; **VIII**: 0.60 $^5J(4\text{-H}, \beta'\text{-H})$, 171.1 $^1J(C^3, 3\text{-H})$, 172.0 $^1J(C^4, 4\text{-H})$.

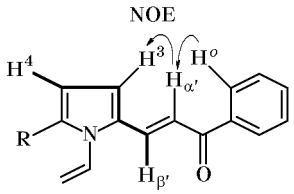
[b] No coupling constant was determined because of signal overlap.

angle ψ; see structure **A**) [2, 10]. This is confirmed by reduction of donor effect of the pyrrole ring on the benzene ring in molecule **VI**: signals from the *ortho*- and *para*-carbon atoms of the benzene ring shift downfield by 1.94 and 0.6 ppm, respectively. An additional shielding of the $C^{\beta}$ nucleus (by 1.89 ppm) may be attributed to increased conjugation with the 1-vinyl group (decrease of the angle φ) due to weakening of steric compression upon rotation of the phenyl ring.

Analysis of various coupling constants (Table 3) provides most information on the steric structure of the compounds under study. The vicinal coupling constant $^3J(\alpha'\text{-H}, \beta'\text{-H})$ for the ketovinyl group of pyrroles **I**–**X** is 15.2–15.3 Hz, indicating that these compounds are *trans* isomer. Direct $^{13}C$–$^1H$ coupling constants in the benzene rings of compounds **I**–**VIII** are as follows: $^1J(C^o, o\text{-H})$ 159.1–159.6, $^1J(C^m, m\text{-H})$ 160.3–161.2, and $^1J(C^p, p\text{-H})$ 160.5–161.6 Hz, and the constant $^4J(3\text{-H}, \beta'\text{-H})$ is equal to 0.60 Hz for all substituted pyrroles **II**–**X**.

Molecules **I**–**X** are also characterized by long-range spin–spin coupling between the 3-H and 4-H protons of the pyrrole ring and β′-H of the ketovinyl group through 4 and 5 bonds, respectively. The latter interaction should be transmitted through a planar zig-zag

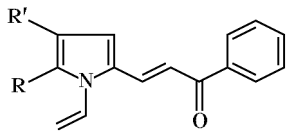
fragment [11, 12] implying *trans*(N)-orientation of the $C^{\beta'}=C^{\alpha'}$ double bond with respect to the pyrrole ring (structure **C**). The predominant *trans*(N)-arrangement of the oxovinyl and 1-vinyl groups is confirmed by the presence of a cross-peak between 3-H and α′-H in the NOESY spectra of all compounds **I**–**X**.



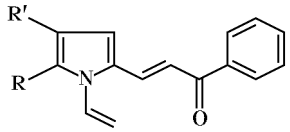

**B**

The coupling constants $^5J$(4-H,β′-H) in molecules **I**, **II**, **IV**, and **X** are similar (Table 3); therefore, we can state that the substituent in position *5* of the pyrrole ring does not affect the configuration of the $C^{\beta'}=C^{\alpha'}$ bond. Coupling between the α′-H and *o*-H protons (formally through 5 bonds) is reliably detected by $^1$H–$^1$H COSYLR experiment [13] (COSY for long-range spin–spin couplings) for pyrroles **I**–**VIII**. The constant $^5J$(α′-H,*o*-H) in the unidimensional $^1$H NMR spectrum is so small that it could not be measured. The interaction α′-H–*o*-H is transmitted through space [14, 15], indicating *trans*-orientation of the phenyl ring with respect to the oxovinyl group (structure **B**). The α′-H and *o*-H protons in pyrroles **I**–**VIII** give cross-peaks in the NOESY spectra.

2-(2-Benzoylethenyl)-1-vinylpyrrole (**I**) shows long-range couplings between the pyrrole ring protons and those of the 1-vinyl group through 4, 5, and 6 bonds (Table 3). An analogous interaction was found previously in 2-substituted 1-vinylpyrroles [1, 16]. Its stereospecificity suggests *trans*-orientation of the vinyl group relative to the 2-substituent in the pyrrole ring. In going to substituted pyrroles **II**–**X**, the long-range coupling between protons of the pyrrole ring and 1-vinyl group disappears, indicating acoplanar orientation of the corresponding molecular fragment [1]. Deviation of the vinyl group from the heteroring plane in molecules **II**–**X** is accompanied by inversion of the relative positions of the $H_A$ and $H_B$ signals (see parameter δ in Table 1) [10]. In addition, the geminal coupling constant $^2J(H_A,H_B)$ in the spectra of **II**–**X** increases (with account taken of its sign). This indicates variation of electron density on the β-carbon atom of the vinyl group. The decrease in the difference between the direct $^{13}$C–$^1$H coupling constants of $C^{\beta}$ in compounds **II**–**X** and **I** (parameter Δ*J* in Table 3) is a function of the dihedral angle between the pyrrole ring and vinyl group planes [10, 17]. As follows from the Δ*J* values for compounds **II**, **III**, **V**–**VII**, and **IX**, this angle does not exceed 60°. Therefore, the lack of symmetry in these compounds gives rise to two possible spatial orientations of the vinyl group (structures **C** and **D**), which cannot be distinguished on the basis of chemical shifts and coupling constants in the $^1$H and $^{13}$C NMR spectra.

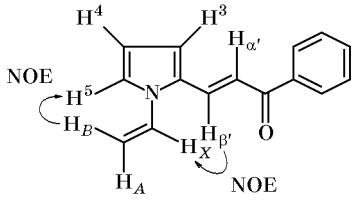



**C**



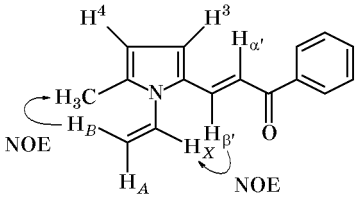

**D**

An additional information can be obtained from analysis of nuclear Overhauser effects (NOE) for protons of compounds **I**–**X**. The NOESY spectrum of pyrrole **I** displays cross-peaks between $H_X$ and β′-H and between $H_B$ and 5-H. These data indicate that the corresponding protons are located spatially close, which is possible when the oxovinyl and 1-vinyl groups are arranged *trans* (structure **E**):

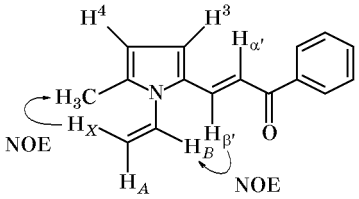



**E**

In the NOESY spectrum of 2-(2-benzoylethenyl)-5-methyl-1-vinylpyrrole (**II**), the $H_B$ proton gives cross-peaks with the 5-$CH_3$ protons and β′-H of the keto-vinyl group. In addition, cross-peaks of $H_X$ with the same protons are obsered (structures **F** and **G**). Such spectral pattern is explained by the existence of molecule **II** in two conformations with *trans*- (**F**) and *cis*-orientations (**G**) of the vinyl and oxovinyl grupp. In conformer **G**, the $H_B$ and β′-H protons, as well as $H_X$ and 5-$CH_3$, are located close to each other,




**F**




**G**

giving rise to the corresponding cross-peaks in the NOESY spectrum. Likewise, short distances between the $H_B$ and 5-$CH_3$ protons and between β′-H and $H_X$ in conformer **F** are responsible for the appearance of cross-peaks between the respective signals. The observed NOESY spectrum of **II** is a superposition of cross-peaks for conformers **F** and **G**. Analogous patterns are also typical of 2-(2-acylethenyl)-1-vinylpyrroles **III**, **V**, **VII**, and **IX**. For example, 2-(2-benzoylethenyl)-1-vinyl-4,5,6,7-tetrahydroindole (**III**) shows NOE for the $H_B$ resonance and the $C^7H_2$ signal, as well as for the β′-H resonance; the presence of cross-peaks between $H_X$ and the above protons indicate the existence of conformational equilibrium like **F**⇄**G**. The situation strongly changes in going to pyrroles **IV**, **VIII**, and **X**. In the NOESY spectrum of 2-(2-benzoylethenyl)-5-phenyl-1-vinylpyrrole (**IV**) we observed only one cross-peak between $H_B$ and β′-H. This means that only one conformer of **IV** exists with *cis*-orientation of the 1-vinyl group with respect to the oxovinyl fragment (structure **D**). Presumably, electrostatic repulsion between the π-systems of the vinyl group and phenyl ring makes the conformation with *trans*-arrangement of the vinyl and oxovinyl groups unfavorable from the viewpoint of energy.

## EXPERIMENTAL

The $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker DPX-250 spectrometer operating at 250.1 and 62.9 MHz, respectively; chloroform-*d* was used as solvent, and hexamethyldisiloxane, as internal reference; sample concentrations were 5–10 wt % for $^{13}C$ and 1 wt % for $^1H$ NMR spectra. Typical parameters of the pulse sequence were as follows: $^1H$: spectral range 4000 Hz, pulse width 7.1 μs (angle 90 deg), acquisition period 1 s, pulse delay 5 s; $^{13}C$: spectral range 15000 Hz, pulse width 4.9 μs (angle 90 deg), acquisition period 0.9 s, pulse delay 7 s. The aromatic carbon signals were assigned using the heteronuclear twodimensional HSQC technique [8], and quaternary carbon signals were identified with the aid of the HMBC technique [9].

2-(2-Benzoylethenyl)-1-vinylpyrroles **I**–**VIII** were synthesized by the procedure reported in [5].

**2-(2-Thenoylethenyl)-1-vinyl-4,5,6,7-tetrahydroindole (IX).** Equimolar amounts of 1-vinyl-4,5,6,7-tetrahydroindole (0.073 g, 0.5 mmol) and thenoylacetylene (0.068 g, 0.5 mmol) were mixed with 1.4 g of silica gel (100/140 μm). The mixture was ground until it became homogeneous and was kept at room temperature with intermittent shaking for 1 h (the mixture turned persistently dark orange). It was then transferred into a column charged with aluminum oxide, and the column was eluted with hexane–ether (2 : 1). A yellow–orange fraction was collected, from which we isolated 0.110 g (78%) of compound **IX** as yellow–orange needles with mp 111–112°C. Found, %: C 72.13; H 6.08; N 4.52; S 10.95; $C_{17}H_{17}NOS$. Calculated, %: C 72.05; H 6.05; N 4.94; S 11.31.

**5-Phenyl-2-(2-thenoylethenyl)-1-vinylpyrrole (X)** was synthesized in a similar way from 0.084 g (0.5 mmol) of 2-phenyl-1-vinylpyrrole and 0.068 g (0.5 mmol) of thenoylacetylene. The mixture was kept for 3 h (until it turned dark orange) and was transferred into a column charged with $Al_2O_3$. The column was eluted with hexane–ether (2 : 1), and a bright yellow fraction was collected. Yield 0.086 g (57%), fine bright yellow needles, mp 117–118°C. Found, %: C 74.63; H 5.20; N 4.77; S 10.47; $C_{19}H_{15}NOS$. Calculated, %: C 74.72; H 4.95; N 4.59; S 10.50.

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