

¹³C–¹³C Spin–Spin Coupling Constants in Structural Studies: XL. Conformational Analysis of *N*-Vinylpyrroles

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Abstract—Conformational analysis of ten *N*-vinylpyrroles was performed on the basis of experimental ¹³C–¹H and ¹³C–¹³C coupling constants and those calculated by high-level quantum-chemical methods, and principal relations between *J*_{CC} and *J*_{CH} values and stereochemical structure of these compounds were revealed.

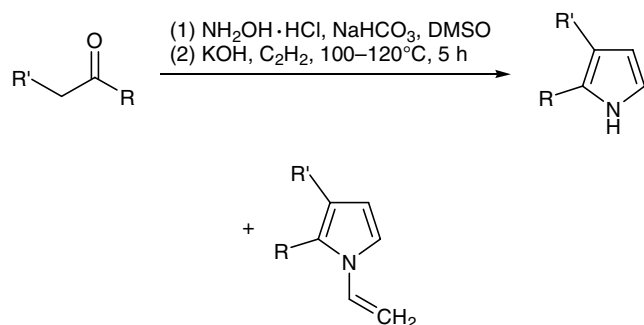
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Persistent interest in pyrrole compounds originates from their unique biological and physical properties; this stimulates search for new methods of building up pyrrole ring. In the recent years, reactions of oximes with acetylene in superbasic media (Trofimov's reaction) have been extensively studied; these reactions lead in one step to the formation of pyrroles and *N*-vinylpyrroles [1]. We have recently developed a novel version of the Trofimov reaction (Scheme 1), which ensures preparation of pyrroles and *N*-vinylpyrroles directly from ketones and acetylene without preliminary isolation and purification of intermediate oximes [2]; this version opens a simple synthetic route to previously inaccessible molecular ensembles that constitute structural fragments of such biologically important compounds as chlorophyll, hemoglobin, vitamin B₁₂, antibiotics, and alkaloids, i.e., substances

responsible for accumulation of solar energy, oxygen transfer in living matter, and other vital processes [3].

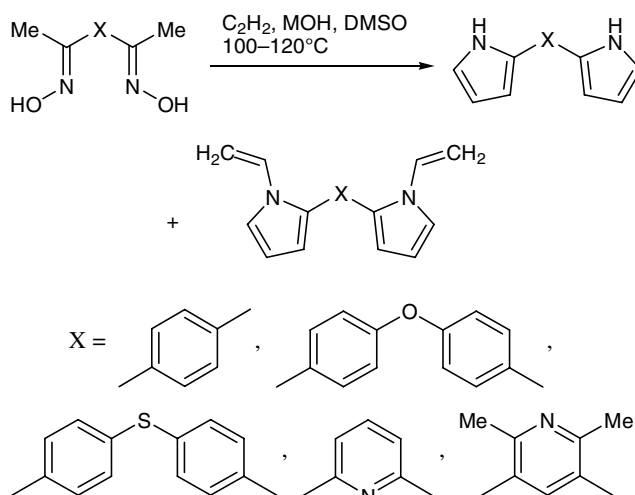
Using diacetyl-substituted benzene, diphenyl ether, diphenyl sulfide, and pyridine derivatives, we have developed a procedure for the synthesis of compounds in which two pyrrole rings are linked through phenylene, oxy- and thiodiphenylene, and pyridinediyl bridges; the procedure is based on the reaction of the corresponding dioximes with acetylene in the presence of superbasic catalysts [4, 5] (Scheme 2). The resulting conjugated bis-pyrroles are promising as precursors of new conducting and electrochromic polypyrrole materials.

Scheme 1.

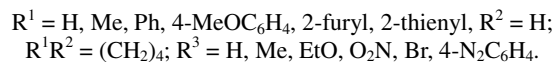
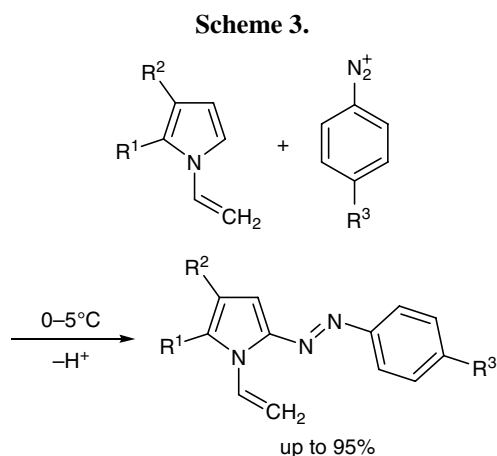


R = Me, Et, *t*-Bu, Ph, 2-thienyl, 2-furyl, R' = H; RR' = (CH₂)₄.

Scheme 2.



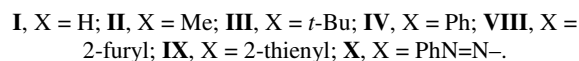
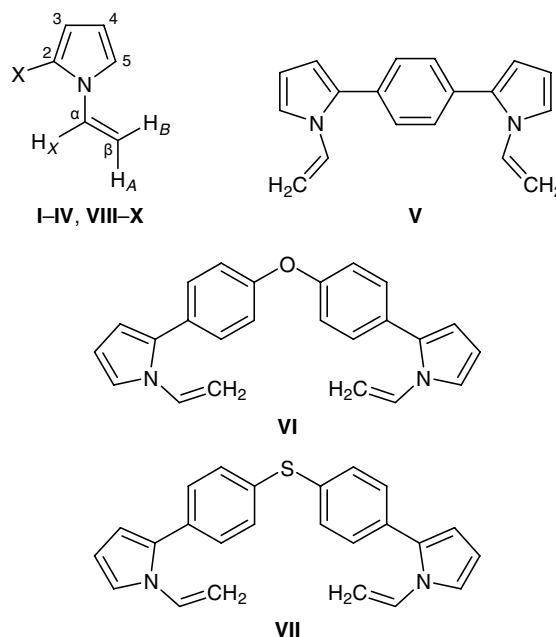
With the goal of extending the synthetic potential of *N*-vinylpyrroles and estimating the relative reactivity of the vinyl group and pyrrole ring therein toward various cationic species, we also examined the reaction of *N*-vinylpyrroles with arenediazonium salts [6]. As a result, we obtained in high yield 2-aryldiazenyl-*N*-vinylpyrroles (Scheme 3) which attract interest from the viewpoint of design of electrochromic devices, optical switchers, materials for nonlinear optics, analytical sensors, and chromogenic agents. 2-Aryldiazenyl-*N*-vinylpyrroles were used to synthesize colored polymers and palladium complexes; the latter showed a high catalytic activity in cross-coupling reactions according to Heck.



High fluorescence quantum yields of bis-pyrroles containing phenylene and hetarylene linkers result mainly from restricted internal rotation of the *N*-vinylpyrrole fragments and considerable deviations from planar structure: up to 20° for the pyrrole rings and 45° for the vinyl groups [4]. Therefore, the importance of studies on stereochemical aspects of the structure and reactivity of *N*-vinylpyrroles is beyond doubt.

In the present work we examined the steric structure of ten 2-substituted *N*-vinylpyrroles **I–X** by analyzing the experimental and theoretically calculated ^{13}C – ^1H and ^{13}C – ^{13}C coupling constants and the potential energy surfaces for internal rotation in their molecules. The coupling constants were calculated in terms of the second-order polarization propagator approximation (SOPPA) [7] with account taken of four contributions: Fermi contact (J_{FC}), spin–dipole (J_{SD}), diamagnetic spin–orbital (J_{DSO}), and paramagnetic spin–orbital (J_{PSO}), using special correlation-consistent Dun-

ning basis sets [8] which were supplemented by the internal correlation functions [9] as described in [10]. The SOPPA method gave good results in the calculation of coupling constants for simplest organic [11] and inorganic molecules [12], polycycloalkanes [13], small heterocycles [14], and Schiff bases [15]. In the present work we were the first to apply this method to a series of aromatic five-membered heterocycles, *N*-vinylpyrroles **I–X**.



First of all, we performed conformational analysis of 2-methyl-*N*-vinylpyrrole (**II**) as a typical representative of this class of compounds. Analysis of the po-

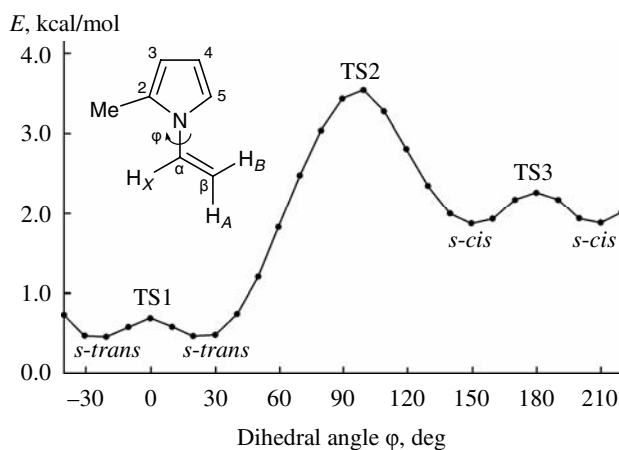


Fig. 1. Potential energy curve for internal rotation of the vinyl group in 2-methyl-*N*-vinylpyrrole (**II**).

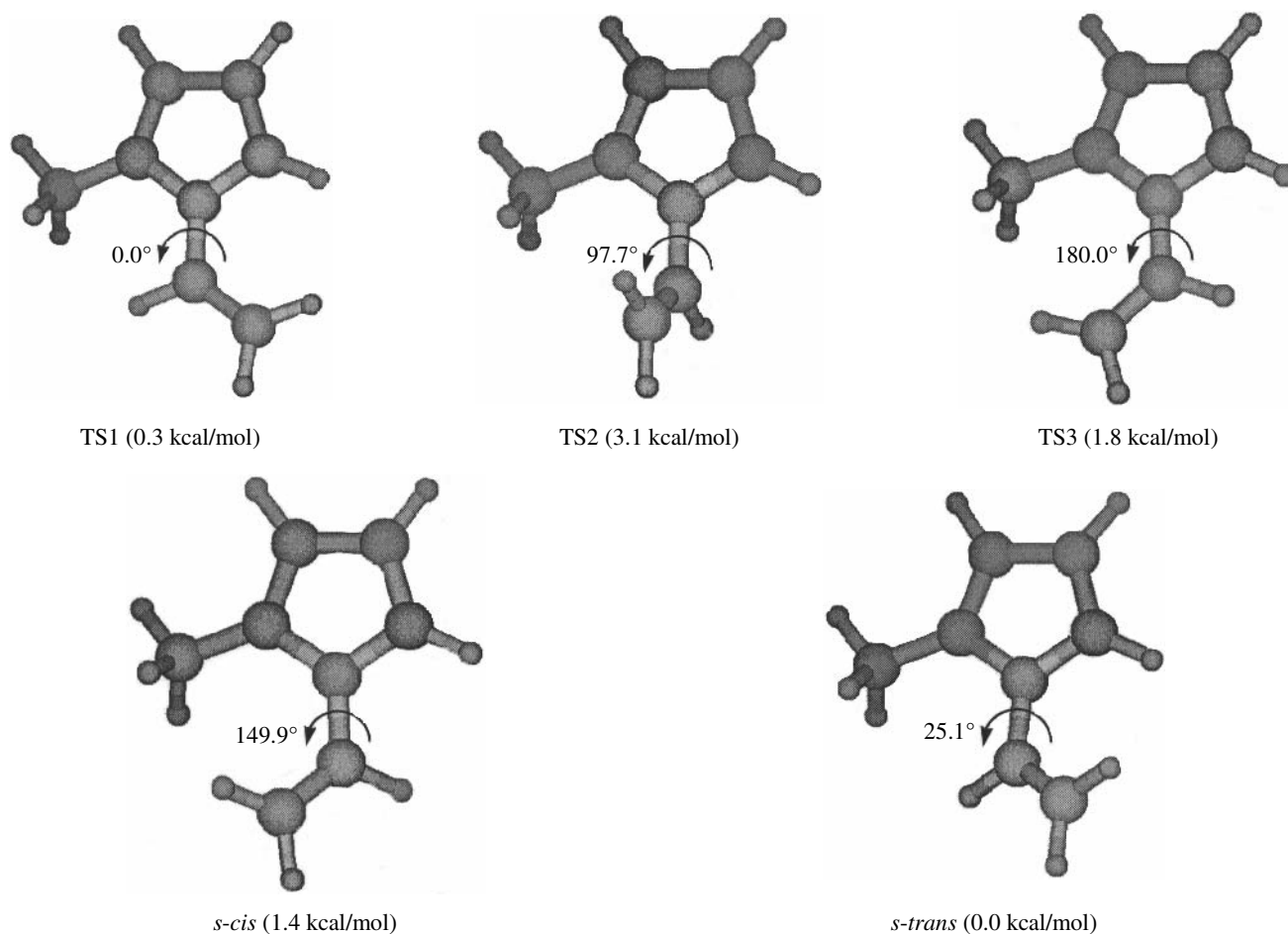


Fig. 2. Rotational conformers and transition states of 2-methyl-*N*-vinylpyrrole (**II**) optimized by the MP2/6-311G* method; the relative energies are given in parentheses.

tential curve for internal rotation in its molecule (calculated by the MP2/6-311G* method with optimization of geometric parameters at each point) revealed

Table 1. ^{13}C NMR spectra (CDCl_3 , 25°C) of *N*-vinylpyrroles **I–X**

Comp. no.	Chemical shifts δ_{C} , ppm					
	C^2	C^3	C^4	C^5	C^{α}	C^{β}
I	118.6	110.1	110.1	118.6	133.0	96.6
II	128.8	108.6	109.7	116.1	130.8	97.6
III	141.4	106.3	108.1	118.8	133.5	99.7
IV	134.2	110.1	110.1	118.2	131.9	98.5
V	133.9	110.3	110.2	118.7	132.1	99.1
VI	133.7	109.9	110.1	118.2	132.0	98.9
VII	133.5	110.4	110.2	118.9	132.0	99.4
VIII	124.5	110.6	110.3	118.7	132.0	99.6
IX	126.5	111.5	110.2	118.5	131.3	99.1
X	145.8	100.2	112.1	120.8	129.9	99.7

five stationary points (Fig. 1): two doubly degenerate minima, *s-cis* and *s-trans*, and three transition states, TS1, TS2, and TS3; the corresponding optimized structures are shown in Fig. 2.

The nature of the conformers and transition states was established by analysis of normal harmonic vibrations. It was found that all vibrational frequencies of the *s-cis* and *s-trans* conformers are real numbers and that the spectra of three transition states (TS1, TS2, and TS3), simulated by the Newton–Rafson algorithm, include imaginary frequencies. The existence of transition states TS1 and TS3 may be attributed to steric interactions in planar conformations, and transition state TS2 is likely to appear as a result of rupture of π – π conjugation between the pyrrole ring and vinyl group when the latter deviates from the pyrrole ring plane (orthogonal conformation).

The ratio of the *s-cis* and *s-trans* conformers in the equilibrium mixture was estimated by analysis of populations of rotational conformations of **II** with

respect to the dihedral angle ϕ at each point (20°C). Summation of the statistical weights of each rotamer, calculated at the MP2/6-311G* level (Fig. 3) gave populations of the *s-cis* and *s-trans* conformers of **II**: 8.8 and 91.2%, respectively.

These results are very consistent with the experimental and calculated ^{13}C – ^{13}C and ^{13}C – ^1H coupling constants. Figure 4 shows the plots of ^{13}C – ^{13}C coupling constants versus dihedral angle ϕ in the molecule of 2-methyl-*N*-vinylpyrrole (**II**). It is seen that the constant $J(\text{C}^\alpha, \text{C}^\beta)$ is the most sensitive to the angle of rotation of the vinyl group about the C^α –N bond. Analysis of populations in terms of the natural bond orbital (NBO) method [16] showed that the sensitivity of $J(\text{C}^\alpha, \text{C}^\beta)$ to ϕ is related to change of the *s* character of the $\text{C}^\alpha=\text{C}^\beta$ bond, which sharply decreases when the vinyl group deviates from the pyrrole fragment, and to weakening of π – π conjugation between the double bond and aromatic pyrrole system. Thus, the coupling constant $J(\text{C}^\alpha, \text{C}^\beta)$ may be used to estimate the dihedral angle between the vinyl group and pyrrole ring in *N*-vinylpyrroles; however, the difference in $J(\text{C}^\alpha, \text{C}^\beta)$ for planar *s-cis* and *s-trans* conformations, resulting from different contributions of spatial interactions between vinyl hydrogen atoms and methylpyrrole fragment, is small (about 1.5 Hz).

Stereochemical dependences of direct ^{13}C – ^1H coupling constants (Fig. 5) are considerably more encouraging. Among these, the strongest relations to ϕ are observed for $J(\text{C}^\alpha, \text{H}_X)$ and $J(\text{C}^\beta, \text{H}_A)$, while the dependence of $J(\text{C}^\beta, \text{H}_B)$ upon ϕ is weaker. Rotation of the vinyl group through an angle of 180° is accompanied by change of $J(\text{C}^\alpha, \text{H}_X)$ and $J(\text{C}^\beta, \text{H}_A)$ by ~6–7 Hz and of $J(\text{C}^\beta, \text{H}_B)$ by ~3 Hz; as above, these variations result from change of the *s* character of the corresponding bond (C^α – H_X , C^β – H_A , or C^β – H_B) due to rotation of the vinyl group about the C^α –N bond. On the other hand, the vicinal coupling constants $J(\text{C}^2, \text{H}_X)$ and $J(\text{C}^5, \text{H}_X)$ show a pronounced Karplus dependence upon the angle ϕ : the difference is 2–3 Hz for the *s-cis* and *s-trans* conformers of 2-methyl-*N*-vinylpyrrole (**II**); therefore, these constants may be used to estimate conformer ratio of *N*-vinylpyrroles.

Thus, statistical analysis of all stereochemical dependences of ^{13}C – ^{13}C and ^{13}C – ^1H coupling constants of 2-methyl-*N*-vinylpyrrole and comparison with the corresponding experimental values showed that this compound exists as an equilibrium mixture of *s-cis* and *s-trans* conformers at a ratio of ~1:9 which is consistent with the ratio calculated by the MP2/6-311G*

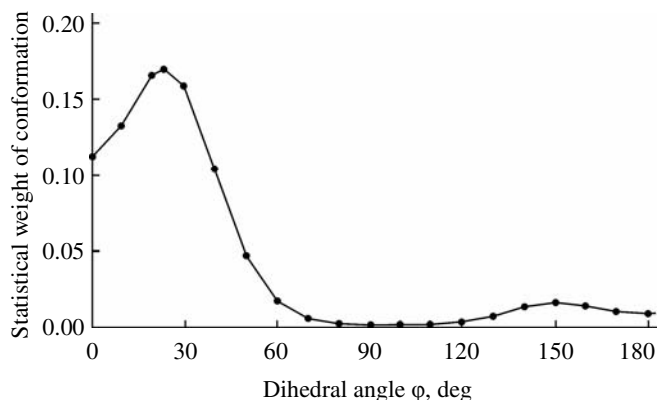


Fig. 3. Statistical distribution of populations of rotational conformers of 2-methyl-*N*-vinylpyrrole (**II**).

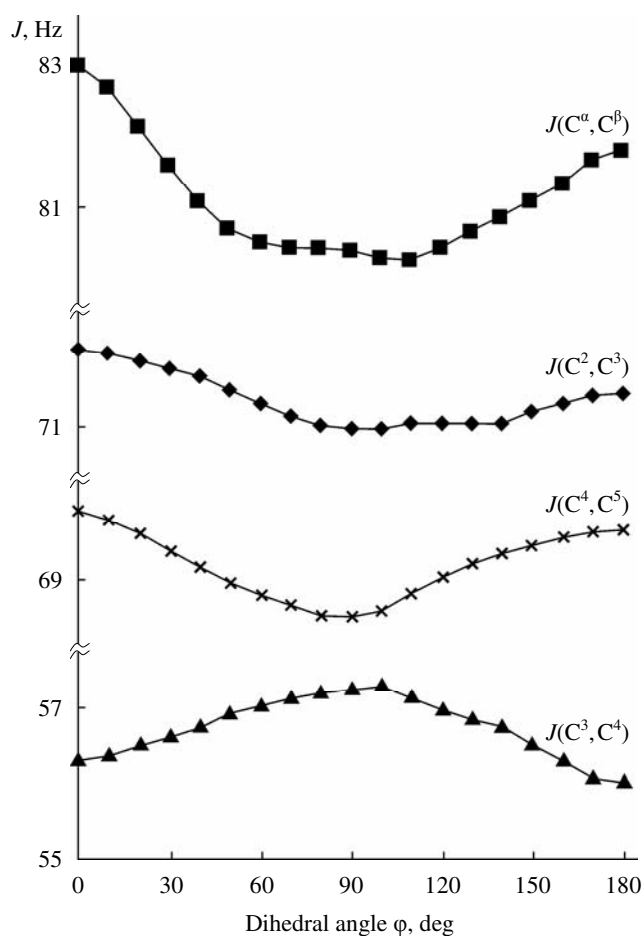


Fig. 4. Plots of ^{13}C – ^{13}C coupling constants versus dihedral angle ϕ in the molecule of 2-methyl-*N*-vinylpyrrole (**II**).

method (see above). Our results also made it possible to estimate the dihedral angle ϕ between the vinyl group and pyrrole ring in each conformer: ~25° for the *s-cis* conformer and ~20° for the *s-trans* conformer (cf. MP2/6-311G* data shown in Fig. 2).

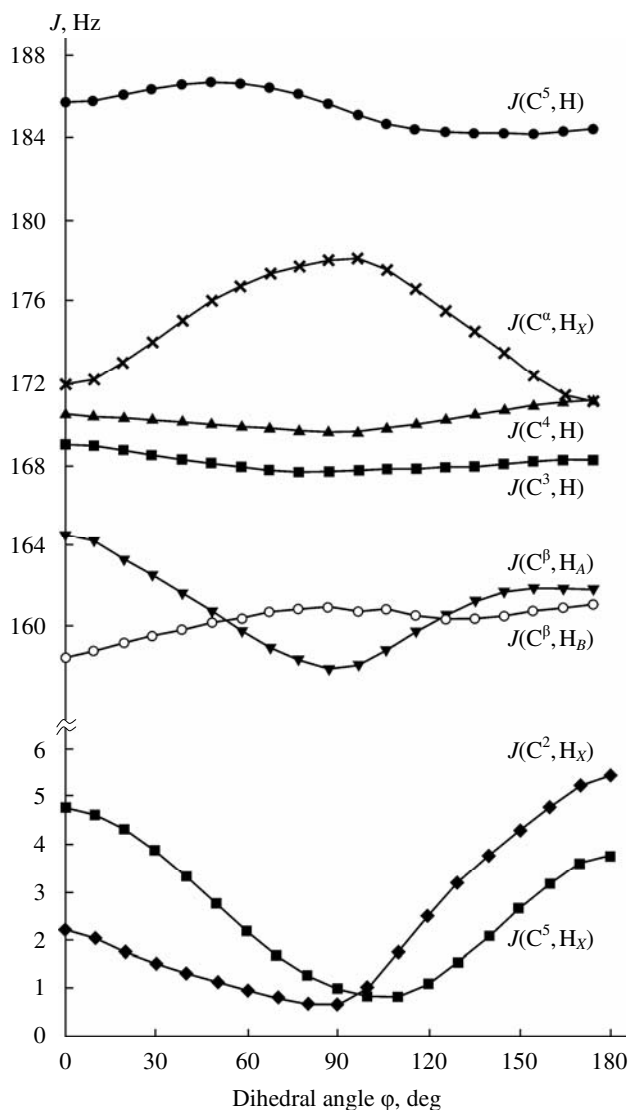


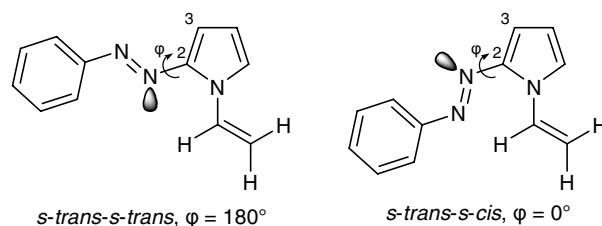
Fig. 5. Plots of ^{13}C – ^1H coupling constants versus dihedral angle φ in the molecule of 2-methyl-*N*-vinylpyrrole (II).

The experimental ^{13}C chemical shifts and ^{13}C – ^{13}C and ^{13}C – ^1H coupling constants of vinylpyrroles I–X are given in Tables 1 and 2. Statistical processing of the experimental J_{CC} and J_{CH} values (Table 2) with account taken of rotamer populations (Fig. 3) and $J_{\text{CC}}-\varphi$ and $J_{\text{CH}}-\varphi$ dependences (Figs. 4, 5) for model 2-methyl-*N*-vinylpyrrole (II) allowed us to perform conformational analysis of the entire series of 2-substituted *N*-vinylpyrroles I–X and estimate the dihedral angles between the vinyl group and pyrrole ring in different conformers of each compound (Table 3). The results showed that the examined compounds exist preferentially as *s-trans* conformers whose fraction is no less than ~90%. Both *s-cis* and *s-trans* conformers are essentially nonplanar, and the vinyl group in most

compounds I–X deviates from the pyrrole ring plane by an angle of ~20–25°. The dihedral angle φ in 2-*tert*-butyl-*N*-vinylpyrrole (III) reaches 35° (*s-trans*) and 45° (*s-cis*). Obviously, the reason is very strong steric interactions between the bulky *tert*-butyl group and hydrogen atoms of the vinyl group in both conformers of III, especially in *s-cis*; correspondingly, the fraction of the latter is as small as 2%.

2-Phenyldiazenyl-*N*-vinylpyrrole (X) prepared by reaction of *N*-vinylpyrrole with benzenediazonium salt [6] attracts specific interest as the first representative of arylazopyrroles. Analysis of the potential energy surface of compound X at the MP2/6-311G* level revealed four stationary points, three of which correspond to ground states (*s-trans-s-trans*, *s-cis-s-trans*, and *s-trans-s-cis*); their optimized structures are shown in Fig. 6. The fourth high-energy *s-cis-s-cis* conformer is not shown in Fig. 6; its relative energy is 6.0 kcal/mol, and it is a transition state. As with 2-methyl-*N*-vinylpyrrole (II) (see above), the structures of three ground-state conformers of X were determined by analysis of normal harmonic vibration frequencies. Both aromatic fragments (benzene and pyrrole rings) in the three conformers are almost coplanar to the N=N bond and hence to each other, while the vinyl group in the predominant *s-trans-s-trans* conformer is turned through an angle of ~25° with respect to the pyrrole ring plane (Fig. 6).

Useful information on rotational conformers of X, arising from rotation of the phenylazo group about the C²–N bond, can be obtained from the $J(\text{C}^2, \text{C}^3)$ values. This coupling constant shows a strong dependence on mutual orientation of the C²–C³ bond and unshared electron pair on the diazenyl nitrogen atom in the α -position with respect to C² (Fig. 7). The reason is well known UEP effect [17] which gives a negative contribution to the coupling constant $J(\text{C}^2, \text{C}^3)$ for the *s-trans-s-trans* conformer and positive contribution for the *s-trans-s-cis* conformer.



The nature of the above effect was considered in detail in a number of studies [18]. The lone electron pair on the imino nitrogen atom gives a positive

Table 2. ^{13}C – ^{13}C and ^{13}C – ^1H coupling constants (Hz) in the ^{13}C NMR spectra (CDCl_3 , 25°C) of compounds I–X

Comp. no.	$J(\text{C}^2, \text{C}^3)$	$J(\text{C}^3, \text{C}^4)$	$J(\text{C}^4, \text{C}^5)$	$J(\text{C}^\alpha, \text{C}^\beta)$	$J(\text{C}^3, \text{H})$	$J(\text{C}^4, \text{H})$	$J(\text{C}^5, \text{H})$	$J(\text{C}^\alpha, \text{H}_X)$	$J(\text{C}^\beta, \text{H}_A)$	$J(\text{C}^\beta, \text{H}_B)$
I	67.7	^a	67.7	77.7	171.4	171.4	185.8	174.1	156.9	163.7
II	69.8	51.0	67.7	77.8	168.8	170.0	185.0	173.1	157.0	163.2
III	69.8	50.5	66.6	77.2	169.5	170.7	184.9	173.5	157.5	162.4
IV	69.3	^b	66.8	77.6	171.5	171.0	185.7	175.1	156.9	163.5
V	69.3	^b	66.6	77.5	171.3	171.7	186.0	174.3	157.1	163.6
VI	69.3	^b	66.5	77.6	171.1	171.7	185.6	176.0	157.1	163.6
VII	69.3	^b	66.5	77.8	171.1	172.0	186.1	176.6	157.2	163.6
VIII	69.6	^b	66.5	77.6	172.8	172.4	186.2	177.4	157.2	163.6
IX	70.2	51.4	66.5	77.7	172.1	172.2	186.3	176.1	157.2	163.6
X	72.8	53.3	64.0	77.6	176.5	173.8	187.6	175.8	157.2	164.1

^a The coupling constant was not determined because of equivalence of the C^3 and C^4 nuclei.^b The coupling constant was not determined because of signal overlap.

through-space contribution to the ^{13}C – ^{13}C coupling constant for the neighboring carbon–carbon bond in the *cis* position. On the other hand, electron density transfer from the nitrogen UEP on the antibonding molecular orbital of the neighboring carbon–carbon bond in the *trans* position (n_σ – σ^* interaction [19]) makes that bond weaker, and the corresponding coupling constant decreases, i.e., the contribution of UEP

to the overall J_{CC} value is negative. The above interactions give rise to a dramatic difference between the $J(\text{C}^2, \text{C}^3)$ values of the *s-trans-s-trans* and *s-trans-s-cis* conformers of **X**, which amounts to almost 10 Hz (Fig. 7). Comparison of the calculated $J(\text{C}^2, \text{C}^3)$ values, ~73 (*s-trans-s-trans*) and ~83 Hz (*s-trans-s-cis*), with that found experimentally, 72.8 Hz, indicates preferential *s-trans-s-trans* conformation of 2-phenyldiazenyl-

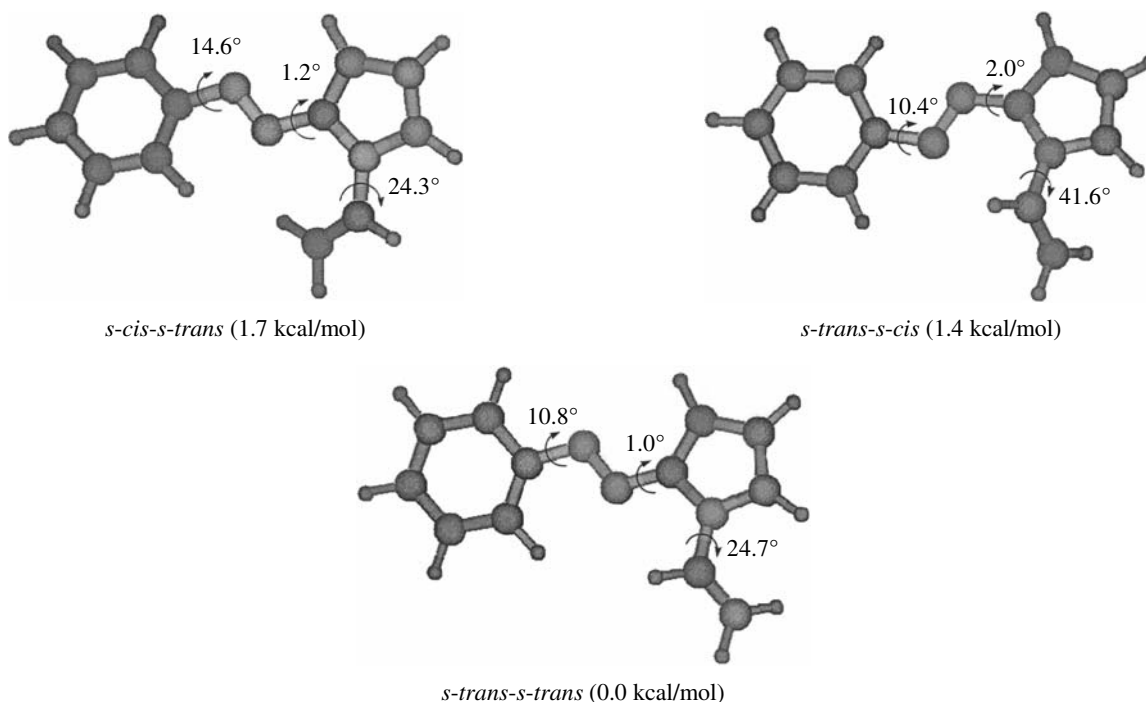
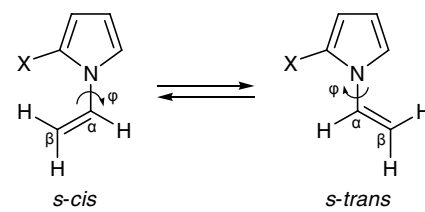
**Fig. 6.** Rotational conformers of 2-phenyldiazenyl-*N*-vinylpyrrole (**X**), optimized by the MP2/6-311G* method; the relative energies are given in parentheses.

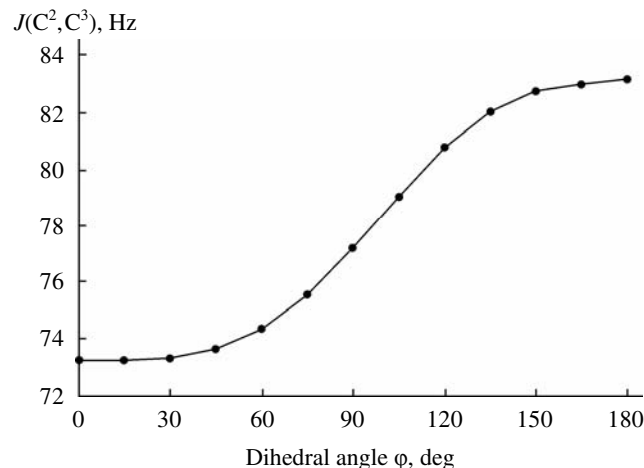
Table 3. Conformational composition of 2-substituted *N*-vinylpyrroles **I–X**


Comp. no.	<i>s-cis</i> Conformer		<i>s-trans</i> Conformer	
	fraction, %	ϕ , deg	fraction, %	ϕ , deg
I	50 ^a	23	50 ^a	23
II	9	30	91	24
III	2	43	98	35
IV	10	25	90	23
V	11	24	89	22
VI	11	24	89	22
VII	11	22	89	21
VIII	11	22	89	21
IX	11	22	89	21
X	8	32	92	25

^a Degenerate exchange.

N-vinylpyrrole (**X**), in keeping with the results of theoretical conformational analysis performed at the MP2/6-311G* level (see above).

We can conclude that our study revealed pronounced stereospecificity of ^{13}C – ^{13}C and ^{13}C – ^1H coupling constants in *N*-vinylpyrroles. These coupling constants are very sensitive to internal rotation of the vinyl group

**Fig. 7.** Plot of the coupling constant $J(\text{C}^2, \text{C}^3)$ versus dihedral angle ϕ in the 2-phenyldiazenyl-*N*-vinylpyrrole (**X**) molecule.

and other substituents in the pyrrole ring, which makes it possible to perform conformational analysis of some interesting *N*-vinylpyrrole derivatives.

EXPERIMENTAL

Pyrroles **I–IV**, **VIII**, and **IX** were synthesized from the corresponding commercially available ketones and acetylene according to the procedures reported in [2]; bis-pyrroles **V–VII** were prepared from the corresponding diketone dioximes and acetylene as described in [4]; 2-phenyldiazenyl-*N*-vinylpyrrole (**X**) was obtained by diazo coupling of *N*-vinylpyrrole with benzenediazonium salt [6].

The ^{13}C NMR spectra were measured at 25°C from 0.1 M solutions in CDCl_3 on a Bruker Avance-400 spectrometer at 101.61 MHz using 10-mm ampoules; hexamethyldisiloxane was added as internal reference. The ^{13}C – ^{13}C coupling constants were measured using INADEQUATE pulse sequence [20] with the following parameters: pulse width 90°, pulse duration 13 μs , scan width 10 kHz, FID record time 6 s, relaxation delay 10 s, characteristic pulse delay 3.6 ms ($J = 70$ Hz), digital resolution 0.05 Hz, accumulation time 4 to 24 h. The ^{13}C – ^1H coupling constants were measured from the ^{13}C NMR spectra recorded without decoupling from protons (broad-band decoupling from protons was periodically switched on during relaxation delays).

Quantum-chemical calculations were performed using GAMESS [21] and DALTON software [22] with either standard built-in basis sets or those modified by the authors (for details, see [10]).

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