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CONFORMATIONAL ANALYSIS OF N-VINYL-2-PHENYLPYRROLE*

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A conformational analysis of N-vinyl-2-phenylpyrrole was undertaken according to the results from experimental measurements and nonempirical quantum-chemical calculation of the high-level $^{13}C–^{1}H$ and $^{13}C–^{13}C$ spin-spin coupling constants. Angular relationships were established in the direct and vicinal $J_{C,C}$ and $J_{C,H}$ constants in the N-vinylpyrrole fragment, making it possible to use them in stereochemical investigations of the vinyl derivatives of pyrrole.

Keywords: N-vinyl-2-phenylpyrrole, conformational analysis, spin-spin coupling constants, second-order polarization propagator approximation (SOPPA).

The reaction of oximes with acetylene in superbasic media, leading to pyrroles and N-vinylpyrroles in a single stage (the Trofimov reaction), has been studied vigorously in recent years [1, 2]. N-Vinyl-2-phenylpyrrole (**1**) is a typical representative of the series of N-vinylpyrrole derivatives, obtained by the Trofimov reaction, that are widely represented in nature (chlorophyll, hemoglobin, vitamin B_{12}, antibiotics, and alkaloids taking part in the fixation of solar energy, the transport of oxygen in living organisms, and other live-supporting processes) and are of interest for the most diverse regions of human activity – from pharmacology to electronics [3]. Of no lesser interest is the stereochemical aspect of the structure of N-vinylpyrroles, which determines their reactivity and characteristics that are important in practical respects.

In the present work a detailed stereochemical investigation of N-vinyl-2-phenylpyrrole was undertaken by theoretical analysis of its potential energy surface of internal rotation and also the results of experimental measurement and nonempirical calculation of the high-level $^{13}C–^{1}H$ and $^{13}C–^{13}C$ spin-spin coupling constants. The theoretical calculation of the spin-spin coupling constants was done by the polarization propagator approach in terms of the second-order polarization propagator approximation (SOPPA) [4] with regard to all four contributions from spin-spin coupling – Fermi contact (J_{FC}), spin-dipole (J_{SD}), diamagnetic spin-orbital (J_{DSO}), and paramagnetic spin-orbital (J_{PSO}) – using the special correlation-consistent basis sets of Dunning [5], extended by functions that take account of internal correlation [6], as described in [7]. The nonempirical high-level SOPPA method recommended itself well for calculations of spin-spin coupling constants in organic molecules of small and medium size [8], which formed the basis of its use in the present work.

* Dedicated to Boris Aleksandrovich Trofimov on his 70th jubilee.

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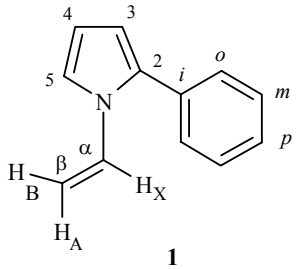
In N-vinyl-2-phenylpyrrole there is internal rotation of the N-vinyl group about the N–C_α bond and of the phenyl group about the C(2)–C(i) bond. According to the results from quantum-chemical calculations at the MP2/6-311G* level in the gas phase on the rotational potential energy surface of the molecule of **1** there were two stable conformers (not containing imaginary frequencies in the harmonic vibrational spectrum), i.e., *s-cis* and *s-trans*, characterized by substantial deviations from the planar structure (Fig. 1). This was due to steric



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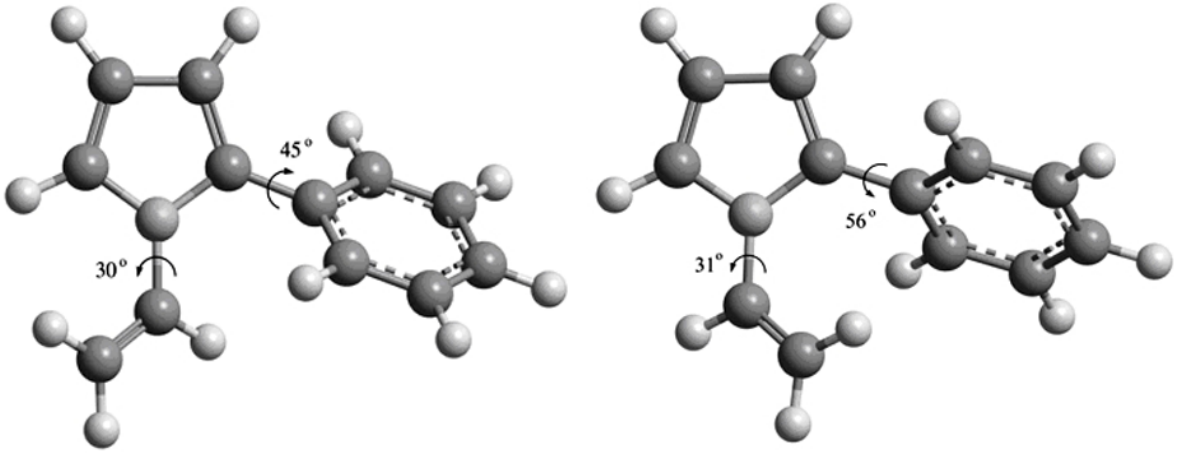
interactions between the hydrogen atoms of the vinyl and phenyl groups in both conformers. Thus, in the preferred *s-trans* conformer the angle between the planes of the pyrrole ring and the N-vinyl group amounts to φ = 30° at an angle of φ = 45° between the planes of the pyrrole ring and the phenyl group, whereas these values in the more high-energy *s-cis* conformer are φ = 31 and 56° respectively with an energy difference of 1.9 kcal/mol between the conformers.



s-trans *s-cis*

Fig. 1. The rotational conformers of N-vinyl-2-phenylpyrrole optimized by the MP2/6-311G* method in the gas phase. Relative total energies: *s-trans* 0.0 kcal/mol, *s-cis* 1.9 kcal/mol.

For a more detailed study of the internal rotation of the vinyl group in the molecule of **1** and for accurate determination of the ratio of its conformers the theoretical curves for the energetics of internal rotation were calculated (Fig. 2). The total energy for the rotation of the vinyl group was calculated with optimization of the geometry in the gas phase by the MP2/6-311G* method with a fixed value for the dihedral angle φ for each 10°. An accurate integral ratio of the *s-trans* and *s-cis* conformers, amounting to 91:1, was obtained from the results of the calculations by integration of the obtained curve for the probability density of the population of the conformations of **1** (Fig. 2*b*).

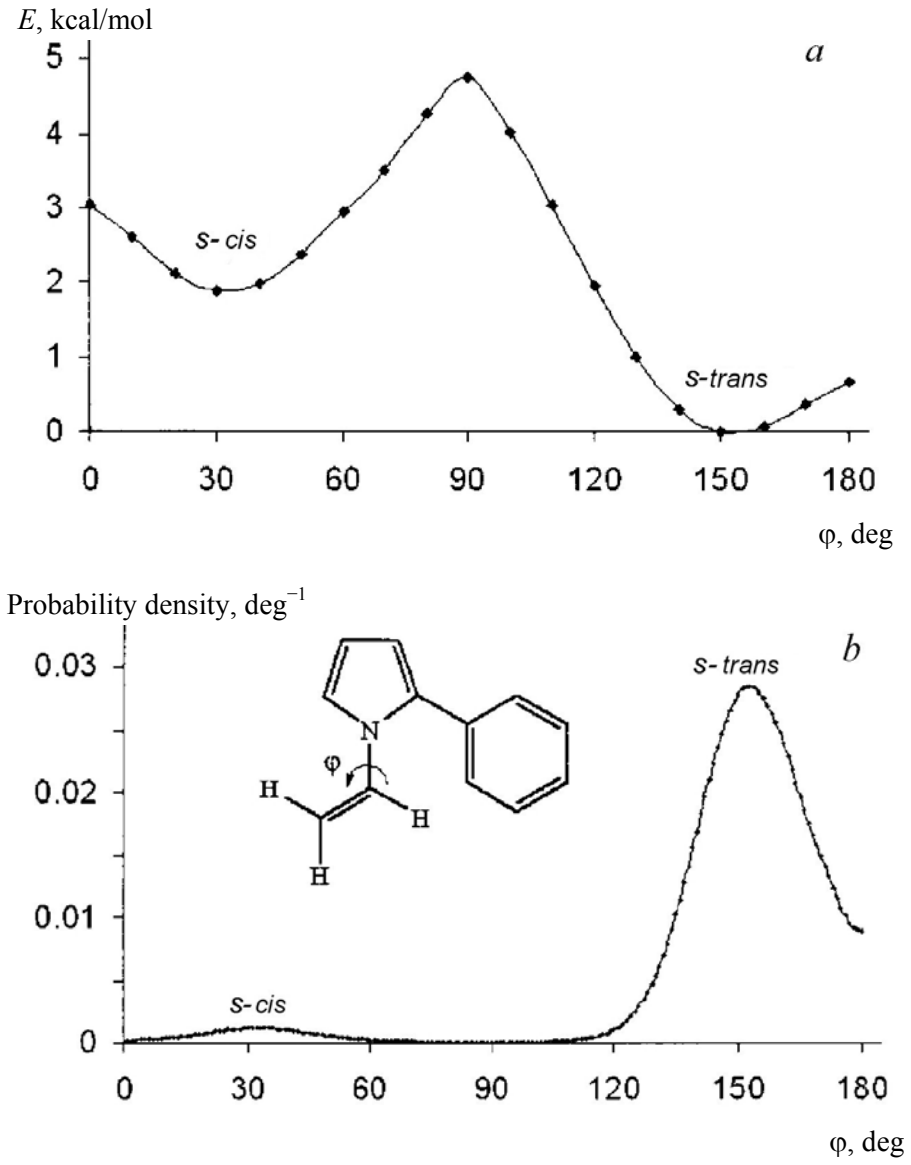


Fig. 2. The potential curve for internal rotation of the vinyl group (*a*) and the curve for the probability density of the population of rotational conformations (*b*) of N-vinyl-2-phenylpyrrole, calculated by the MP2/6-311G* method; φ is the dihedral angle.

Table 1 contains the direct and vicinal $^{13}C–^{1}H$ and $^{13}C–^{13}C$ spin-spin coupling constants, calculated by the SOPPA method in the preferred *s-trans* conformer of N-vinyl-2-phenylpyrrole, and their experimental values determined from the 2D HMBC and 2D INADEQUATE spectra. (The use of the last method is illustrated in Fig. 3.)

It is seen from the data in the table that for all the examined direct and vicinal $^{13}C–^{1}H$ and $^{13}C–^{13}C$ spin-spin coupling constants excellent agreement is observed between their calculated and experimental values (as a rule within a range of less than 0.5% of the total constant), demonstrating the adequacy of the employed level of the nonempirical theory.

In this work we were also interested in the angular relationships of the $^{13}C–^{1}H$ and $^{13}C–^{13}C$ spin-spin coupling constants of the N-vinylpyrrole fragment for internal rotation about the N–C_α bond, which were calculated in terms of the SOPPA method for the case of N-vinyl-2-phenylpyrrole (Figs. 4 and 5). As follows from these data, all the examined direct and vicinal $^{13}C–^{1}H$ and $^{13}C–^{13}C$ constants of the N-vinylpyrrole fragment exhibit clearly defined angular relationships due to internal rotation of the vinyl group (discussion of their nature falls outside the scope of this article), and this makes it possible to use the above-mentioned spin-spin coupling constants for conformational analysis of a wide range of N-vinylpyrroles and their derivatives.

TABLE 1. The $^{13}C–^{13}C$ and $^{13}C–^{1}H$ Spin-Spin Coupling Constants of N-Vinyl-2-phenylpyrrole Calculated by the SOPPA Method* and Determined Experimentally

SSCC	$J_{calc.}$, Hz					J_{exp}, Hz
	J_{PSO}	J_{DSO}	J_{SD}	J_{FC}	J	
^{1}J(C-2,C-3)	0.31	-6.45	1.57	72.28	67.71	68.3
^{1}J(C-4,C-5)	0.25	-6.49	1.61	71.28	66.65	66.8
$^{1}J(C_\alpha,C_\beta)$	0.18	-8.27	3.26	82.18	77.35	77.6
$^{1}J(C\text{-}2,C_i)$	0.37	-1.52	0.59	67.84	67.28	66.7
$^{1}J(C_i,C_o)$	0.29	-6.04	1.14	62.46	57.85	57.5
$^{1}J(C_o,C_m)$	0.23	-6.21	1.15	61.96	57.13	56.8
$^{1}J(C_m,C_p)$	0.22	-6.14	1.16	60.53	55.77	55.6
^{1}J(C-3,H)	0.96	0.38	0.27	167.98	169.59	170.0
^{1}J(C-4,H)	0.86	0.41	0.25	168.84	170.36	170.5
^{1}J(C-5,H)	1.03	0.20	0.26	184.90	186.39	185.7
$^{1}J(C_m,H)$	0.84	0.23	0.17	158.69	159.93	161.3
$^{1}J(C_p,H)$	0.83	0.25	0.19	158.71	159.98	160.9
$^{1}J(C_o,H)$	0.96	0.13	0.19	159.04	160.32	158.8
$^{1}J(C_\alpha,H_X)$	1.04	0.01	0.21	175.42	176.68	175.1
$^{1}J(C_\beta,H_A)$	0.58	0.59	0.24	161.42	162.83	163.5
$^{1}J(C_\beta,H_B)$	0.64	0.58	0.25	155.03	156.50	156.9
$^{3}J(C_i,C_p)$	0.02	0.47	1.62	8.23	10.34	10.3
$^{3}J(C_o,C_m)$	0.01	0.42	1.54	7.47	9.44	9.0
$^{3}J(C\text{-}3,C_o)$	0.01	0.11	-0.13	2.09	2.08	2.1
$^{3}J(C_m,C\text{-}2)$	-0.03	0.03	0.06	4.54	4.60	4.2
$^{3}J(C\text{-}5,C_i)$	-0.05	0.01	-0.01	1.39	1.34	1.6
$^{3}J(C\text{-}2,C_\beta)$	-0.06	0.27	0.21	1.98	2.40	2.7
$^{3}J(C\text{-}5,C_\beta)$	0.01	-0.02	0.13	2.07	2.19	2.4
$^{3}J(C\text{-}2,H_X)$	0.19	-0.16	-0.01	1.33	1.35	1.3
$^{3}J(C\text{-}5,H_X)$	-0.43	0.16	0.01	4.00	3.74	4.4

* For the preferred *s-trans* conformer, see Fig. 1.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX-400 and AVANCE-400 spectrometers (400 and 100 MHz) in ampules with external diameters of 5 and 10 mm at 25°C in 10% solutions in CD_3OD or DMSO-d_6 with the addition of HMDS as internal standard. The $^{13}C–^{13}C$ spin-spin coupling constants were measured with the INADEQUATE pulse sequence and the following parameters: width of spectrum 6 kHz; pulse length 13.5 μsec; relaxation time 4 sec; readout time of decay of free induction signal 4 sec; digital

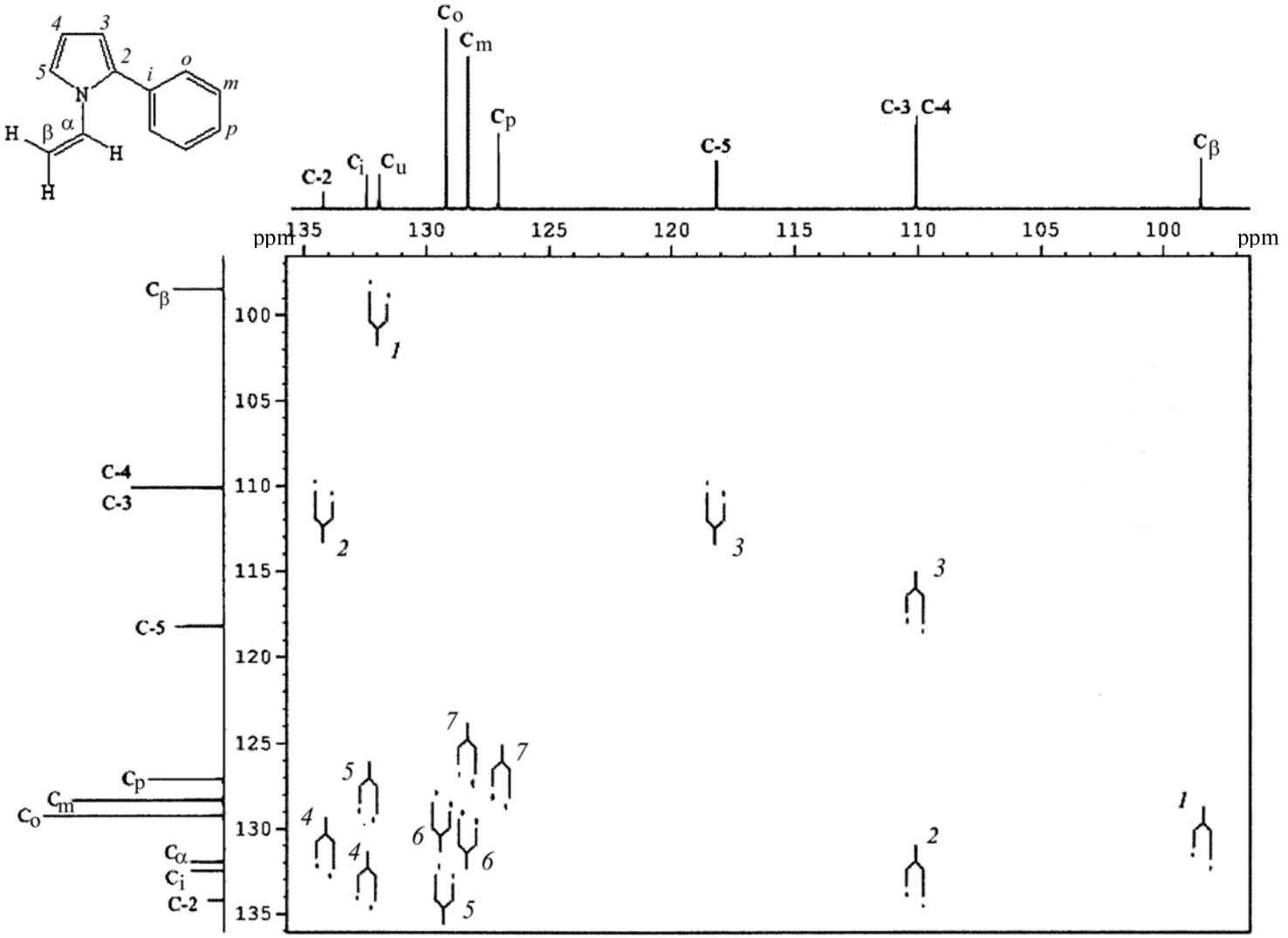


Fig. 3. ^{13}C Spectrum 2D INADEQUATE of N-vinyl-2-phenylpyrrole in $CDCl_3$ (100.61 MHz). *1* – $^1J(C_\alpha,C_\beta)$, *2* – ^1J(C 2,C-3), *3* – ^1J(C-4,C-5), *4* – ^1J(C-2,C_i), *5* – $^1J(C_i,C_o)$, *6* – $^1J(C_o,C_m)$, *7* – $^1J(C_m,C_p)$.

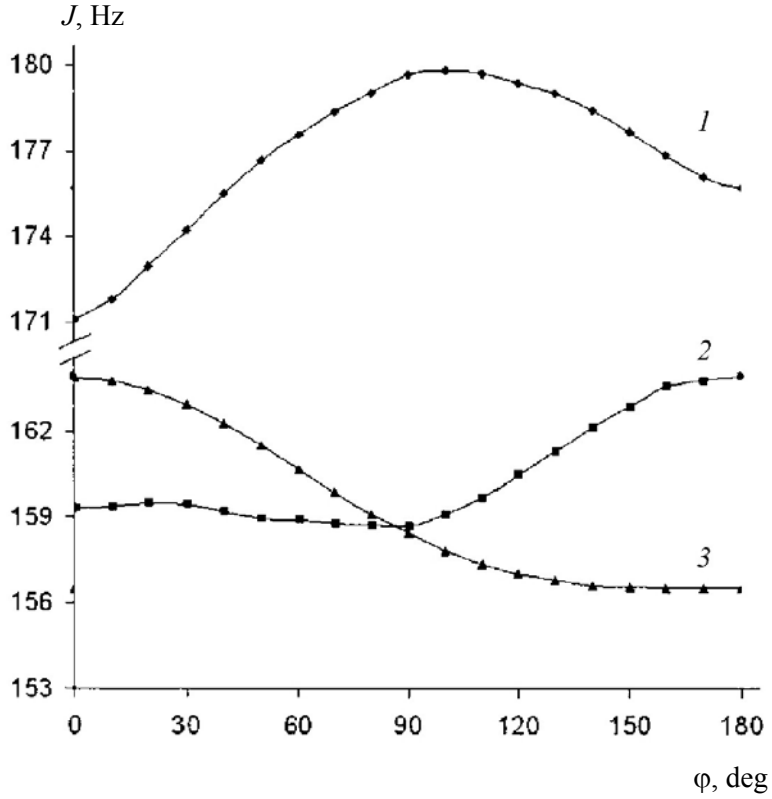


Fig. 4. The angular relationships of the direct $^{13}C–^{1}H$ spin-spin coupling constants of the vinyl group for internal rotation about the N–C_α bond in N-vinyl-2-phenylpyrrole, calculated by the SOPPA method: *1* – $^{1}J(C_\alpha,H_X)$; *2* – $^{1}J(C_\beta,H_A)$; *3* – $^{1}J(C_\beta,H_B)$.

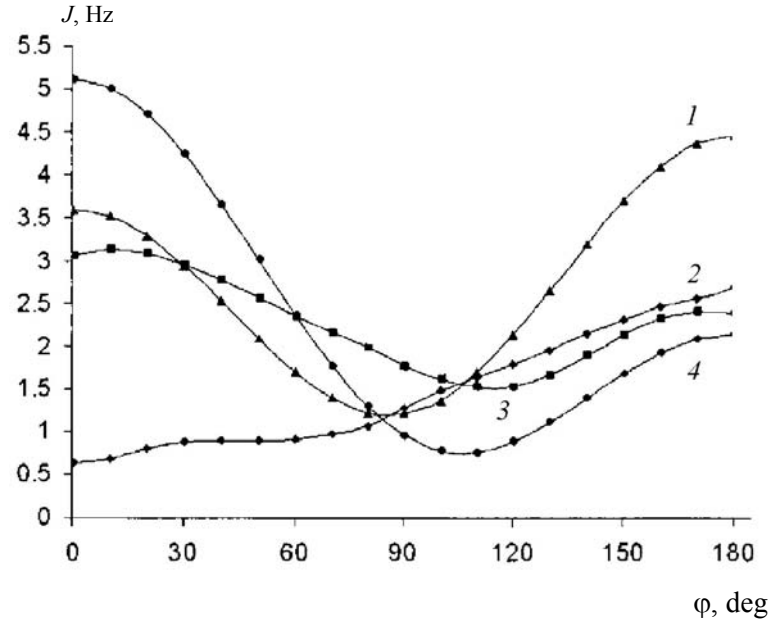


Fig. 5. The angular relationships of the vicinal $^{13}C–^{1}H$ and $^{13}C–^{13}C$ spin-spin coupling constants for internal rotation about the N–C_α bond in N-vinyl-2-phenylpyrrole, calculated by the SOPPA method: *1* – $^{3}J(C\text{-}5,H_X)$; *2* –$^{3}J(C\text{-}2,C_\beta)$; *3* $^{3}J(C\text{-}5,C_\beta)$; *4* $^{3}J(C\text{-}2,H_X)$.

resolution 0.1 Hz/point; accumulation time from 6 to 24 h. The $^{13}C–^{1}H$ spin-spin coupling constants were measured from the proton-coupled ^{13}C NMR spectra with periodic inclusion of broadband proton decoupling during the relaxation times with the above-mentioned spectral parameters.

The quantum-chemical calculations were carried out with the GAMESS [9] and DALTON [10] software. The geometric parameters were optimized and the total energies were calculated at the level of second-order MP2/6-311G** perturbation theory, and the $^{13}C–^{13}C$ spin-spin coupling constants were calculated in terms of second-order polarization propagator theory SOPPA using standard library basis sets or basis sets modified by the present authors, the detailed specification of which was presented in [11].

The N-vinyl-2-phenylpyrrole (**1**) was obtained from acetophenone oxime and acetylene in the presence of the superbase system KOH–DMSO [3].

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