ROTATIONAL ISOMERISM IN 1-VINYLPYRAZOLES AND 1-VINYLIMIDAZOLES FROM ^1H AND ^{13}C NMR DATA AND QUANTUM-CHEMICAL CALCULATIONS

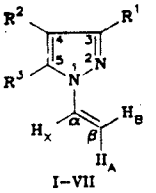
A. V. Afonin, D. K. Danovich, V. K. Voronov, L. A. Es'kova, L. V. Baikalova, and E. S. Domina

UDC 543.422.25:547.772.04

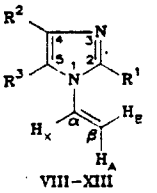
A quantitative evaluation of the percentages of rotational isomers of 1-vinylpyrazoles and 1-vinylimidazoles was made on the basis of an analysis of the ^1H and ^{13}C NMR spectral parameters and quantum-chemical calculations. It is shown that the populations of the s-cis-($N_{(2)}$, $N_{(3)}$) and s-trans-($N_{(2)}$, $N_{(3)}$) forms in both the 1-vinylpyrazole and in the 1-vinylimidazole are approximately equal.

The known data on the existence of rotational isomers in 1-vinylpyrazoles are qualitative in character. 1-Vinylpyrazoles that do not have a substituent in the 5 position of the ring exist in the form of mixtures of s-cis-($N_{(2)}$) and s-trans-($N_{(2)}$) conformers, while the introduction of a methyl group into the indicated position stabilizes the s-cis-($N_{(2)}$) form [1, 2]. Rotational isomerism in 1-vinylimidazoles has not been studied. In the present research we made a quantitative evaluation of the populations of the rotational isomers in 1-vinylpyrazoles and 1-vinylimidazoles, in analogy with the previously studied N-vinyltetrazoles [3].

1-Vinylpyrazoles and 1-vinylimidazoles were synthesized by the methods in [4, 5], respectively. We recorded the ^1H and ^{13}C NMR spectra of 1-vinylpyrazoles I-VII and 1-vinylimidazoles VIII-XIV (Table 1).



I–VII



VIII–XIII

Compound	R^1	R^2	R^3	Compound	R^1	R^2	R^3	Compound	R^1	R^2	R^3
I	H	H	H	VI	CH_3	H	CH_3	X	H	CH_3	H
II	H	Br	H	VII	CH_3	NO_2	CH_3	XI	H	H	CH_3
III	H	NO_2	H	VIII	H	H	H	XII	$CH_2OCH=CH_2$	H	H
IV	CH_3	H	H	IX	CH_3	H	H	XIII	H	Ph	Ph
V	H	H	CH_3								

It was established that an increase in the population of s-cis-($N_{(2)}$) conformation in 1-vinylpyrazoles (in the case of introduction of a substituent into the 5 position of the ring) is accompanied by an increase in the relative chemical shift (CS) of the β protons of the vinyl group ($\Delta\delta = \delta H_A - \delta H_B$) and an increase in the geminal $^2J_{AB}$ spin-spin coupling constant (SSCC) [1]. This occurs due to the developing [in the s-cis-($N_{(2)}$) conformation] closeness of the unshared pair of electrons of the $N_{(2)}$

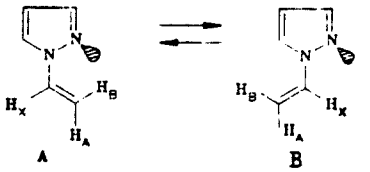
Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1346-1351, October, 1990. Original article submitted November 30, 1988.

0009-3122/90/2610-1121$12.50

TABLE 1. ^1H and ^{13}C NMR Spectra of the Vinyl Group of 1-Vinylpyrazoles I-VII and 1-Vinylimidazoles VIII-XIII

Compound	δ, ppm			Δδ, ppm	J, Hz						ΔJ, Hz
	H_A	H_B	H_X		H_AH_B	H_3H_X	H_4H_X	$C_\beta H_A$	$C_\beta H_B$	$C_\alpha H_X$	
I	4,76	5,43	7,00	0,67	−1,2	0,30	0,30	163,9	159,3	177,9	4,6
II	4,87	5,47	6,98	0,60	−1,5	0,30	—	164,5	159,6	180,4	4,9
III	5,12	5,76	7,01	0,64	−1,7	0,30	—	165,4	160,8	183,4	4,6
IV	4,66	5,35	6,88	0,69	−1,1	—	0,30	163,6	158,7	176,7	4,9
V	4,75	5,60	6,88	0,85	−0,3	0,70	0	162,9	161,3	174,9	1,6
VI	4,66	5,50	6,80	0,84	−0,3	—	0	162,5	161,0	173,9	1,5
VII	5,06	5,83	6,89	0,77	−0,6	—	—	164,0	162,7	178,9	1,3
VIII	4,78	5,19	6,83	0,41	−1,6	—	0,35	164,9	157,5	178,0	7,4
IX	4,79	5,10	6,84	0,31	−1,3	—	0,60	164,5	157,5	176,5	7,0
X	4,79	5,16	6,81	0,37	−1,6	—	—	164,9	157,5	177,2	7,4
XI	4,95	5,30	6,76	0,35	−1,3	—	0	164,4	157,7	177,3	6,7
XII	4,84	5,18	6,96	0,34	−1,5	—	0,55	164,2	157,5	178,9	6,7
XIII	4,88	5,34	6,54	0,46	−1,4	—	—	164,6	158,0	179,4	6,6

atom to the HB proton (see A), which ensures an additional weak field shift of the H_B signal and a positive contribution to the $^2J_{AB}$ SSCC [1, 6]. The difference in the Δδ and $^2J_{AB}$ values in the 5-unsubstituted I-IV and the 5-substituted (V-VII) 1-vinylpyrazoles is evident (see Table 1). In the first case the Δδ parameter is 0.10-0.25 ppm lower and the $^2J_{AB}$ SSCC is 0.5-1.4 Hz higher than in the second case. However, the Δδ and $^2J_{AB}$ values can be used only for a qualitative evaluation of the ratio of the populations of the conformers and not for a quantitative evaluation. The Δδ value is subjected to the influence of the magnetic anisotropy of the ring and the substituents [3, 7], while the $^2J_{AB}$ SSCC depends on the electronegativity of the substituents in the ring [8]. In this connection, changes in the Δδ and $^2J_{AB}$ values are possible without a change in the conformations of the I-VII molecules. Thus, the Δδ parameters in 5-unsubstituted 1-vinylpyrazoles I-IV vary within the limits of 0.1 ppm, while the $^2J_{AB}$ SSCC vary within the range of 0.6 Hz.



The magnetic anisotropy of the ring and the electronegativity of the substituent do not affect the difference in the direct SSCC of the β carbon atom of the vinyl group ($\Delta J = {}^1J_{C\beta H_A} - {}^1J_{C\beta H_B}$) [2]. In addition, the ΔJ parameters in 1-vinylpyrazoles I-VII are sensitive to the type of rotational isomer (A or B). In the s-cis-($N_{(2)}$) conformation an additional positive contribution through space to the $^1J_{C\beta H_B}$ SSCC arises from the unshared pair of the $N_{(2)}$ atom, whereas this does not occur in the s-trans-($N_{(2)}$) conformation [2, 3]. The difference in the ΔJ values for I-IV and V-VII is 3 Hz or greater. The ΔJ parameter is stable in both 5-unsubstituted I-IV and in 5-substituted V-VII 1-vinylpyrazoles (variations $\Delta J \leq 0.3$ Hz, Table 1) and can serve for the quantitative evaluation of the populations of the s-cis-($N_{(2)}$) and s-trans-($N_{(2)}$) conformations. From relationship (1), which we derived in [3], we evaluate the percentage of the s-trans conformation in 1-vinylpyrazole I:

$$n_{trnas} = (\Delta J_{obs} - \Delta J_{cis})/(\Delta J_{trans} - \Delta J_{cis}) = (4{,}6-1{,}5)/(7{,}4-1{,}5) \approx 0{,}53, \quad (1)$$

where n_{trans} is the percentage of the s-trans form, ΔJ_{obs} is the observed ΔJ value in 1-vinylpyrazole, and ΔJ_{cis} and ΔJ_{trans} are the ΔJ values adopted for the s-cis and s-trans conformations, respectively.

The ΔJ_{cis} value was assumed to be equal to the ΔJ parameter in 1-vinyl-5-methylpyrazole (which exists only in the s-cis conformation [1, 2]). The ΔJ_{trans} value was set equal to the ΔJ parameter in 1-vinylimidazole VIII (since VIII does not contain an additional contribution to the $^1J_{C_\beta H_\beta}$ SSCC because of the remoteness of the $N_{(3)}$ atom [9]). Evaluation from relationship (1) provides evidence for the approximately equal populations of the conformations under discussion in 1-vinylpyrazole I.

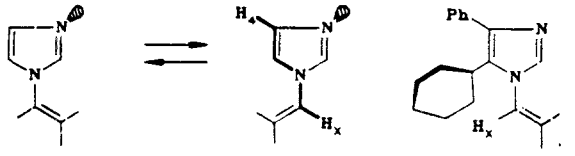
Considering the approximate character of the evaluation that we made, its authenticity should be confirmed by an independent method. For these purposes one can use the stereospecificity of the long-range spin-spin coupling (SSC) between the ring protons and the vinyl group. The observed long-range SSC between the H_3, H_4, and H_X protons through five bonds (see Table 1) is effectively transmitted through the close-to-planar zigzag fragment [10-12], i.e., only in the s-cis (A) and s-trans

(B) conformations, respectively. In conformity with this, on passing from 1-vinylpyrazole I to its 5-methyl-substituted derivative V the constant of long-range SSC between the H_3 and H_X protons ($^5J_{H_3H_X}$, Table 1) increases from 0.30 to 0.70 Hz, while the constant of long-range SSC between the H_4 and H_X protons ($^5J_{H_4H_X}$) decreases from 0.30 Hz to zero. Having made assumptions similar to those used in the derivation of formula (1) we find

$$n_{trans} = (^5J_{cis} - {}^5J_{obs}) / (^5J_{cis} - {}^5J_{trans}) = (0{,}70 - 0{,}30) / (0{,}70 - 0) \approx 0{,}57, \quad (2)$$

where n_{trans} is the fraction of the s-trans form, $^5J_{obs}$ is the observed $^5J_{H_3H_X}$, value in 1-vinylpyrazole, and $^5J_{cis}$ and $^5J_{trans}$ are the $^5J_{H_3H_X}$, values adopted for the s-cis and s-trans conformations of 1-vinylpyrazole. Evaluation from relationship (2) also provides evidence regarding the approximately equal populations of the s-cis and s-trans conformations for pyrazole I. It should be noted that the quantitative evaluations of the percentages of the s-trans conformer in I made on the basis of relationships (1) and (2) differ little. This confirms the mutual reliability of the evaluations made. For all of the 5-substituted I-IV the ΔJ parameter and the $^5J_{H_3H_X}$, SSCC are virtually invariable. This means that the percentage of the s-trans form in I-IV is almost constant.

In imidazoles VIII-XIII the range of change in the $\Delta\delta$, $^2J_{AB}$, and ΔJ values is much smaller than in pyrazoles I-VII (Table 1). The unshared pair of the $N_{(3)}$ atom of VIII-XIII is spatially remote from the H_B proton in both the s-cis-($N_{(3)}$) (C) and s-trans-($N_{(3)}$) (D) conformations, and it therefore does not affect the spectral parameters mentioned above. The certain increase in the $^2J_{AB}$ SSCC and the decrease in $\Delta\delta$ and ΔJ parameters when a substituent is introduced into the 2 and 5 position of the imidazole ring should be linked with an increase in the torsion angle about the N–C_α bond [7, 13]. The $\Delta\delta$, $^2J_{AB}$, and ΔJ parameters are unsuitable for the conformational analysis of imidazoles VIII-XIII.



C D E

However, for the quantitative evaluation of the percentages of the rotational isomers in vinylimidazoles VIII-XIII one can, in analogy with I-VII, use the stereospecificity of the constants of long-range SSC between the ring protons and the vinyl group. In VIII, IX, and XII there is a long-range SSC between the H_4 ring proton and the proton of the vinyl group H_X ($^5J_{H_4H_X}$ = 0.35-0.60 Hz, Table 1). The coupling under discussion in the case of vinylimidazoles VIII-XIII exists only in the s-trans conformation (through the zigzag fragment, see D). The successive decrease in the $^5J_{H_4H_X}$ SSCC in the series 1-vinyl-2-methylimidazole (IX), 1-vinylimidazole (VIII), and 1-vinyl-5-methylimidazole (XI) from 0.60 to 0.35 and then to 0 Hz reflects a transition from the stabilized s-trans conformation (in IX) to the stabilized s-cis conformation (in XI). From relationship (3) for vinylimidazole VIII we find

$$n_{trans} = (^5J_{obs} - {}^5J_{cis}) / (^5J_{trans} - {}^5J_{cis}) = (0{,}35 - 0) / (0{,}60 - 0) \approx 0{,}58. \quad (3)$$

Thus, a close-to-equal percentage of the s-cis and s-trans forms is characteristic for imidazole VIII.

The parameters of the PMR spectra of the vinyl group of 1-vinyl-4,5-diphenylimidazole (XIII) have an interesting peculiarity. The signal of the H_X proton in it is shifted appreciably to strong field relative to I-XII (0.2-0.5 ppm, Table 1). This shift is due to the shielding effect of the magnetic anisotropy of the aryl ring [14] on the H_X proton through space. It can be realized in the case of an s-cis orientation of the vinyl group relative to the substituents in the ring vis-à-vis a substantially noncoplanar orientation of the imidazole and aryl rings (see E).

For a theoretical substantiation of rotational isomerism in the molecules of the series under discussion we performed a quantum-chemical calculation of 1-vinylpyrazole I and 1-vinylimidazole VIII by the AM-1 method [15]. The geometries of the I and VIII molecules were optimized for the s-cis and s-trans conformations. Then, at intervals of 15° we calculated the potential energy of rotation of the vinyl group about the N–C_α bond (Table 2). For vinylpyrazole I and vinylimidazole VIII there are two energy minima in the case of rotation of the vinyl group. They correspond to torsion angles φ of 0° (the s-cis conformation) and 180° (the s-trans conformation). From 0 to 90° the potential energy of rotation increases monotonically, whereas from 90 to 180° it decreases monotonically. The dependence of the potential energy of rotation on torsion angle φ is represented by potential $E(\varphi)$ expanded into a limited Fourier series:

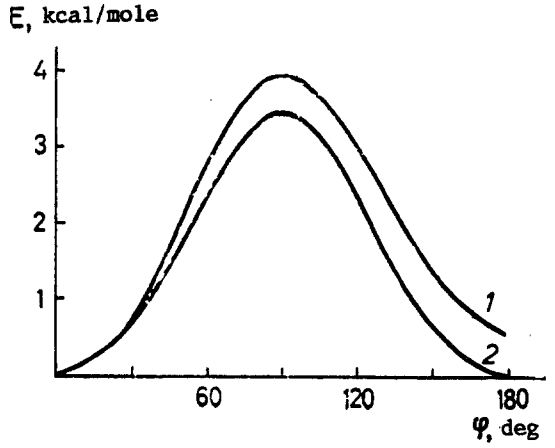


Fig. 1. Dependence of the potential energy of rotation about the N–C_α bond for I (1) and VIII (2).

TABLE 2. Potential Energies of Rotation About the N–C_α Bond for 1-Vinylpyrazole (I) and 1-Vinylimidazole (VIII)*

Compound	E, kcal/mole, for torsion Angle												
	0	15	30	45	60	75	90	105	120	135	150	165	180
I	0	0,17	0,68	1,58	2,51	3,45	4,04	3,79	3,08	2,17	1,33	0,81	0,66
VIII	0	0,16	0,67	1,47	2,35	3,11	3,49	3,11	2,35	1,46	0,65	0,14	−0,03

*For the s-cis conformation ($\varphi = 0$) the E value was assumed to be equal to zero.

Table 3. Coefficients (V_n) of Expansion of the Dependence of the Potential Energy of Rotation of I and VIII into a Fourier Series

Compound	V_1	V_2	V_3	V_4
I	0,768	3,636	−0,148	−0,311
VIII	−0,020	3,438	−0,008	0,263

$$E(\varphi) = \sum_{i=1}^{n} (V_i/2)\,(1-\cos i\varphi). \qquad (4)$$

In the case of I and VIII dependence (4) can be approximated satisfactorily by the first four terms of the expansion. Coefficients V_1-V_4 for I and VIII were determined (Table 3). For pyrazole I, which has an asymmetrical dependence of the potential energy of rotation, both the even and odd members of Fourier series (4) are significant. An almost symmetrical dependence of the potential energy of rotation for imidazole VIII is described chiefly by the even-numbered terms of Fourier series (4) (see Table 3). The dependences of E on the torsion angle are represented graphically in Fig. 1. In Fig. 1 it is clearly seen that only the s-cis and s-trans conformations, which are separated by a barrier to internal rotation of 3-4 kcal/mole, are stable for both vinylpyrazole I and vinylimidazole VIII. A similar form of the dependence of E was obtained for methyl vinyl ether [16] and methyl vinyl sulfide [17].

It follows from the calculated data (Table 2) that the heats of formation of the s-cis and s-trans conformers of VIII are virtually the same (0.03 kcal/mole). A small energic preferableness of the s-cis conformer (0.65 kcal/mole) was obtained for

pyrazole I from the calculations. However, in a qualitative respect, the calculated data (considering that they correspond go the state of the molecules in the gas phase) are in complete agreement with the conclusions regarding the approximately equal populations of the s-cis and s-trans conformations in I and VIII obtained on the basis of experimental evaluations.

EXPERIMENTAL

The PMR spectra were recorded with a Tesla BS-497 spectrometer (100 MHz). The ^{13}C NMR spectra were obtained with a Tesla BS-567 A spectrometer (25.1 MHz). The solvent was $CDCl_3$, and the internal standard was hexamethyldisiloxane (HMDS). The concentration of the samples was 5% for PMR, as compared with 30% for ^{13}C NMR. The proton-coupled ^{13}C NMR spectra were obtained under "Gated decoupling" conditions [18]. The method used to analyze the spin systems of the ^{13}C isotopomers of the vinyl group of the investigated compounds was described in [3]. The measurements were made at room temperature.

LITERATURE CITED

1. L. A. Es'kova, V. K. Voronov, E. S. Domnina, and G. G. Skvortsova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 5, 1012 (1985).
2. A. V. Afonin, V. K. Voronov, L. A. Es'kova, E. S. Domnina, E. V. Petrova, and O. A. Zasyadko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 1, 202 (1987).
3. A. V. Afonin, L. I. Vereshchagin, S. R. Buzilova, A. K. Bogens, Yu. V. Brekhov, and O. A. Zasyadko, *Khim. Geterotsikl. Soedin.*, No. 12, 1662 (1989).
4. G. G. Skvortsova, E. S. Domnina, L. A. Shestova, and V. K. Voronov, *Khim. Geterotsikl. Soedin.*, No. 9, 1247 (1976).
5. M. F. Shostakovskii, G. G. Skvortsova, N. P. Glazkova, and E. S. Domnina, *Khim. Geterotsikl. Soedin.*, No. 6, 1070 (1969).
6. A. V. Afonin, L. A. Es'kova, V. K. Voronov, E. S. Domnina, L. V. Baikalova, and E. V. Petrova, *Khim. Geterotsikl. Soedin.*, No. 4, 499 (1988).
7. M. V. Sigalov, G. A. Kalabin, A. I. Mikhaleva, and B. A. Trofimov, *Khim. Geterotsikl. Soedin.*, No. 3, 328 (1980).
8. R. Knorr, *Tetrahedron*, **37**, 929 (1981).
9. A. V. Afonin, D. K. Danovich, V. K. Voronov, L. A. Es'kova, L. V. Baikalova, and S. R. Buzilova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 4, 872 (1988).
10. J. R. Peat and W. F. Reynolds, *Can. J. Chem.*, **52**, 2403 (1974).
11. W. J. E. Parr, R. E. Wasylishen, and T. Schaefer, *Can. J. Chem.*, **54**, 3216 (1976).
12. A. V. Afonin, Z. V. Stepanova, V. K. Voronov, and A. V. Vashchenko, *Khim. Geterotsikl. Soedin.*, No. 10, 1422 (1987).
13. A. V. Afonin, M. V. Sigalov, V. K. Voronov, E. Yu. Shmidt, and B. A. Trofimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 6, 1418 (1987).
14. R. A. Pascal and R. B. Grossman, *J. Org. Chem.*, **52**, 4616 (1987).
15. M. J. S. Dewar, E. G. Zoeblisch, and E. F. Healy, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
16. F. Bernardi, N. D. Epiotis, R. L. Yates, and H. B. Schlegel, *J. Am. Chem. Soc.*, **98**, 2385 (1976).
17. J. Kao, *J. Am. Chem. Soc.*, **100**, 4685 (1978).
18. P. E. Hansen, *Progr. NMR Spectrosc.*, **14**, 175 (1981).