^{1}H- and ^{13}C-NMR STUDY OF ROTATIONAL ISOMERISM IN N-VINYLTETRAZOLES

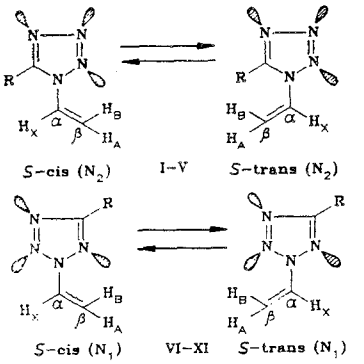
A. V. Afonin, L. I. Vereshchagin, S. R. Buzilova,
A. K. Bogens, Yu. V. Brekhov, and O. A. Zasyadko

UDC 543.422.25:547.796.1:
541.634

The ^{1}H- and ^{13}C-NMR spectral parameters of N-vinyltetrazoles have been analyzed. It has been found that rotational isomerism is inherent to 1- and 2-vinyltetrazoles. A quantitative estimate of the ratio of rotational isomers has been made. In the case of 1-vinyltetrazoles, introduction of a substituent to the 5-position in the tetrazole ring stabilizes the trans-orientation of the vinyl group relative to the substituent, while in the case of 2-vinyltetrazoles the presence of a substituent in the 5-position of the ring essentially does not affect the conformer population.

We have previously studied rotational isomerism in 1-vinylpyrazoles [1, 2] and 1-vinyl-1,2,4-triazoles [3]. The relative populations of the s-cis-($N_{(2)}$) and s-trans-($N_{(2)}$) conformations differ greatly in the case of 1-vinylpyrazoles versus 1-vinyl-1,2,4-triazoles [1-3]. Continuing our systematic investigation of rotational isomerism in N-vinylazoles, we have now studied the ^{1}H- and ^{13}C-NMR spectra of N-vinyltetrazoles.

N-Vinyltetrazoles were synthesized according to the procedure described in [4]. We recorded their NMR spectra, and have summarized the ^{1}H- and ^{13}C-NMR spectral parameters for the vinyl groups in vinyltetrazoles I-XI in Table 1. The chemical shift (CS) values for the β-carbon atom in the vinyl group in compounds I-III and V-XI are in the range 108.14 to 114.11 ppm. The increased shielding of this carbon atom, relative to the carbon atom in ethylene (the CS of the carbon atom in ethylene is equal to 123.3 ppm [5]) is observed in all of the N-vinyltetrazoles examined. This provides evidence for efficient conjugation of the vinyl group with the tetrazole ring [6]. The relatively large range of CS values for C_β (~6 ppm) can be attributed to transmission of the electronic effect across the tetrazole ring to the vinyl group [7]. This is possible due to the predominance of planar conformations for N-vinyltetrazoles I-XI: in the case of 1-vinyltetrazoles I-V the s-cis($N_{(2)}$)- and s-trans($N_{(2)}$)-conformers, in the case of 2-vinyltetrazoles VI-XI the s-cis($N_{(1)}$)- and s-trans($N_{(1)}$)-conformations.



I R=H; II R=CH_3; III R=CH=CH_2; IV R=NH_2; V R=CF_3;
VI R=H; VII R=CH_3; VIII R=CH_2Cl; IX R=Ph; X R=CH=CH_2; XI R=CF_3

We can draw conclusions concerning the conformer ratio in 1- and 2-vinyltetrazoles based on analysis of their ^{1}H-NMR spectra. In the case of the s-cis-conformations in 1-vinyltetrazoles I-V the vinyl group proton H_B is in spatial proximity to the unshared pair of electrons

Irkutsk Polytechnical Institute, Irkutsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1662-1667, December, 1989. Original article submitted April 4, 1988; revision submitted October 4, 1988.

0009-3122/89/2512-1385$12.50

TABLE 1. ^1H- and ^{13}C-NMR Spectral Parameters for the Vinyl Group in N-Vinyltetrazoles

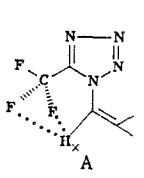
Compound	δ, ppm					J, Hz				
	H_A	H_B	H_X	Δδ	C_β	$^2J_{AB}$	$^1J_{C_\beta H_A}$	$^1J_{C_\beta H_B}$	$^1J_{C_\alpha H_X}$	ΔJ
I	5,44	6,01	7,36	0,57	109,49	−2,1	166,0	161,6	187,7	4,4
II	5,42	6,04	7,12	0,62	110,38	−1,55	165,7	162,7	184,6	3,0
III	5,47	6,10	7,07	0,63	111,77	−1,4	166,1	163,1	185,1	3,0
IV	5,35	5,83	6,89	0,48	—	−1,6	—	—	—	—
V	5,68	6,31	7,21	0,63	114,41	−2,05	166,6	163,9	190,3	2,7
VI	5,41	6,24	7,56	0,83	109,15	−1,65	165,1	163,4	188,1	2,0
VII	5,32	6,13	7,47	0,81	108,14	−1,5	161,9	163,1	187,3	1,8
VIII	5,43	6,23	7,51	0,80	109,64	−1,7	165,4	163,4	188,6	2,0
IX	5,37	6,25	7,55	0,88	108,48	−1,4	165,2	163,3	187,8	1,9
X	5,40	6,20	7,57	0,80	108,52	−1,4	165,7	163,7	187,7	2,0
XI	5,61	6,37	7,59	0,76	111,75	−2,1	166,6	164,1	191,2	2,5

on the $N_{(2)}$ nitrogen atom. In analogy with the behavior observed in the case of 1-vinylpyrazoles and 1-binyl-1,2,4-triazoles, this should lead to an additional downfield shift of the signal due to H_B, reflected in an increased relative CS value for the β-protons in the vinyl group ($\Delta\delta = \delta H_B - \delta H_A$ [1, 3]). Furthermore, the proximity of the unshared electron pair to the H_B proton should result in an additional positive contribution to the geminal coupling constant (SSCC) $^2J_{AB}$ [1]. In this way, therefore, the higher population of the s-cis-conformation in the series I-V should be accompanied by higher Δδ and $^2J_{AB}$ SSCC parameter values.

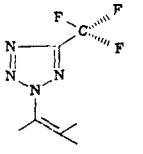
In the transition from 1-vinyltetrazole (I) to its 5-substituted derivatives II, III, and V, the Δδ parameter increases in value from 0.57 to 0.62-0.63 ppm (Table 1). Symbatic changes are also observed in the absolute values of the CS for H_A and H_B in the range 0.2-0.3 ppm, due to the electronic effect of a substituent in the ring [8]. The 0.05-0.06 ppm increase in the parameter Δδ due to introduction of a substituent in the 5-position of the tetrazole ring is associated as well with an increase in the amount or fraction of the s-cis-($N_{(2)}$)-conformer, which is stabilized in compounds II, III, and V by the steric effect of a substituent in the ring. The increase in the Δδ parameter in vinyltetrazoles II and III relative to compound I is accompanied by an increase in the $^2J_{AB}$ geminal SSCC value of 0.6-0.7 Hz (see Table 1), reflecting an additional positive contribution to this SSCC from the unshared electron pair on the nitrogen atom acting through space to shift the equilibrium in favor of the s-cis conformer. In compound V the positive contribution due to the unshared electron pair on the nitrogen atom on the $^2J_{AB}$ SSCC value is compensated for by a negative contribution due to the presence of an acceptor (electron withdrawing) substituent (CF_3) [9].

The anomalously low value of Δδ (0.48 ppm) in 1-vinyl-5-aminotetrazole (IV) stands out in contrast to the trends outlined above. The presence of the amino group in this compound sets up an asymmetrical electrical field, which exerts a selective effect on the CS of the β-carbons in the vinyl group [10, 11]. This may serve as a secondary factor governing the anomalously low value of Δδ in compound IV.

The PMR spectrum of 1-vinyl-5-trifluoromethyltetrazole (V) exhibits long-range spin-spin coupling (SSC) between the fluorine nuclei and the vinyl group proton H_X ($^5J_{H_XF} = 0.85$ Hz, Fig. 1a). This significant long-range SSC between the fluorine nuclei and a proton is transmitted through space [12], and can appear only when the nuclei approach each other within a distance of 2-3 Å [13]. The presence of long-range SSC between fluorine and H_X thus provides evidence in favor of the s-cis($N_{(2)}$)-conformation in vinyltetrazole V, since this is the only conformer featuring the required spatial proximity of the interacting nuclei (A). In the isomeric analog, 2-vinyl-5-trifluoromethyltetrazole (XI), the CF_3 group and the vinyl group are spatially separated or distant (B), and long-range SSC between the fluorine nuclei and the vinyl group protons is not observed (Fig. 1b).



A



B

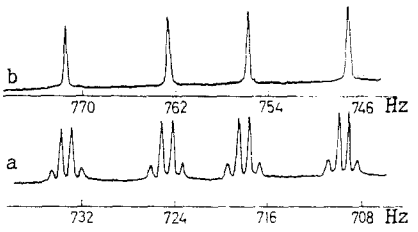
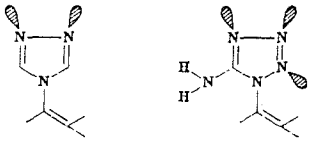


Fig. 1. ^{1}H-NMR spectral fragment (in $CDCl_3$, relative to TMS, 100 MHz operating frequency). Vinyl group H_X proton signal: a) in 1-vinyl-5-trifluoromethyltetrazole (V); b) in 2-vinyl-5-trifluoromethyltetrazole (XI).

A quantitative estimate of the ratio of rotational isomers in 1-vinyltetrazole (I) can be made based on the values of the direct $^{13}C-^1H$ SSCC for the vinyl group (the splitting pattern of the ^{13}C nuclear signals for the vinyl group, arising from spin-spin coupling with the vinyl group protons, has been presented in the literature [14]). The spatial proximity of the $C_\beta-H_B$ bond to the unshared electron pair on the nitrogen atom $N_{(2)}$ in the s-cis conformation gives rise to a supplementary positive contribution to the $^1J_{C_\beta H_B}$ SSCC [2, 14, 15]. A 1-2 Hz increase in the value of the SSCC $^1J_{C_\beta H_B}$ relative to compound I, due to a larger population of the s-cis conformation, is observed in all of the 5-substituted 1-vinyltetrazoles II, III, V. Since the absolute value of the $^1J_{C_\beta H_B}$ SSCC depends on the electronic effect of the substituent in the ring, a quantitative measure of this contribution can be obtained from the difference in the direct $^{13}C-^1H$ SSCC for C_β in the vinyl group ($\Delta J = {}^1J_{C_\beta H_A} - {}^1J_{C_\beta H_B}$) [2, 15]. The value of this difference parameter ΔJ decreases from 4.4 to 2.7-3.0 Hz in the transition from vinyltetrazole I to its 5-substituted derivatives II, III, and V. It follows, therefore, that the value of ΔJ can be assumed to be equal to 3.0 Hz for the s-cis conformation. In the case of the s-trans conformation in compound I there is no contribution to the $^1J_{C_\beta H_B}$ SSCC due to the separation of the unshared electron pair on the $N_{(2)}$ nitrogen atom. Thus, the value of ΔJ for the s-trans-conformation in compound I can be assumed to be equal to that observed in the isostructural analog 1-vinyl-1,3,4-triazole (ΔJ = 6.7 Hz), in which the unshared electron pairs on the nitrogen atoms are spatially removed or distant from the vinyl group (cf. structure C).



C D

Based on these considerations, the following equation or ratio can be postulated to permit a quantitative estimate of the population of the s-trans conformation:

$$n_{trans} = \frac{\Delta J_{obs} - \Delta J_{cis}}{\Delta J_{trans} - \Delta J_{cis}} = \frac{4.4 - 3.0}{6.7 - 3.0} = 0.38, \quad (1)$$

in which n_{trans} is the concentration of the s-trans form; ΔJ_{obs} is the observed value of ΔJ for 1-vinyltetrazoles; and ΔJ_{cis} and ΔJ_{trans} are the values of ΔJ inferred for the s-cis and s-trans conformations, respectively.

Using this estimate [Eq. (1)], we conclude that there is a limited predominance of the s-cis conformer relative to the s-trans conformer in compound I. In this regard 1-vinyltetrazole is analogous to 1-vinyl-1,2,4-triazole, but different from 1-vinylpyrazole [1-3].

The ^{1}H- and ^{13}C-NMR spectral data are consistent with the presence in 1-vinyltetrazole of two conformers, s-cis($N_{(2)}$)- and s-trans($N_{(2)}$)-; introduction of a substituent in the 5-position locks it in the s-cis form.

The stereochemical properties of 1-vinyltetrazoles IV and V are such that their molecular structures result in spatial proximity of the H_X proton and a heteroatom (in the case of compound V a fluorine atom; in the case of compound IV a nitrogen atom; structures A and D, respectively). According to the data presented in a series of studies [16-18], this structural feature should lead to an anomalous downfield shift (~1-2 ppm) of the proton located in proximity to the heteroatom, which can be attributed to the formation of a weak intramolecular hydrogen bond of the type C–H...X. However, an additional downfield shift of the H_X proton signal is not observed in molecules IV and V. Thus, in 1-vinyl-5-trifluoromethyltetrazole (V) the H_X signal is shifted only 0.09 ppm downfield relative to the 5-methyl ana-

logue (II). In 1-vinyl-5-aminotetrazole (IV) the resonance signal due to H_X actually experiences an upfield shift (0.2 ppm) relative to other 5-substituted 1-vinyltetrazoles II and III (Table 1). This suggests the absence of this type of C–H...X interaction in these compounds. Spatial proximity of a proton and heteroatom by itself is not responsible for an anomalous downfield shift of a proton signal (contrary to the assumptions relied on in [19]). A specific type of C–H...X interaction is required for this (anomalous shift).

Spatial proximity of the unshared electron pair on the nitrogen atom and the H_B proton is present in both planar conformations of the 2-vinyltetrazoles VI-XI. In accord with the data obtained in our previous studied [14], the proximity effect of the higher-energy unshared electron pair on the $N_{(1)}$ nitrogen atom in the spectral parameters $\Delta\delta$, $^2J_{AB}$, and ΔJ should be more pronounced or intense than the effect due to the lower-energy unshared electron pair on the $N_{(3)}$ nitrogen atom. The observed increase in the $\Delta\delta$ parameter by 0.2 ppm, and concomitant decrease in the ΔJ parameter by 1 Hz in the transition from 1-vinyltetrazoles II, III, V to the 2-vinyltetrazoles VI-XI (Table 1) can be rationalized by assuming that in compounds VI-XI the s-cis forms are populated substantially. The change in the $^2J_{AB}$ SSCC values in compounds VI-XI, from −1.4 to −2.1 Hz, can be interpreted in terms of the electronic effect of a substituent in the 5-position of the ring, since the $^2J_{AB}$ values are correlated with the CS values of the C_β atom, which are known to reflect an electronic effect of a ring substituent [20]:

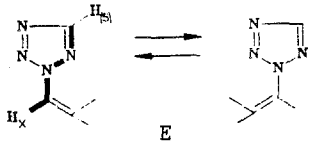
$$^2J_{AB} = -0.193\delta C_\beta + 19.453 \quad (r=0.967,\ s=0.067,\ n=6). \tag{2}$$

A similar linear correlation with the CS values of the C_β atom is observed for both the H_A proton chemical shifts and the direct $^1J_{C_\alpha H_X}$ SSCC values in compounds VI-XI [Eqs. (3) and (4), respectively]; this allows us to conclude that these parameters or functions are sensitive to the electronic effect of the substituent in the ring:

$$\delta H_A = 0.073\delta C_\beta - 2.599 \quad (r=0.981,\ s=0.020,\ n=6); \tag{3}$$

$$^1J_{C_\alpha H_X} = 1.060\delta C_\beta + 72.582 \quad (r=0.992,\ s=0.180,\ n=6). \tag{4}$$

A quantitative estimate of the ratio of s-cis- and s-trans-conformers in 2-vinyltetrazoles VI-XI can be obtained based on analysis of the long-range SSC between the $H_{(5)}$ ring proton and the H_X vinyl group proton, which can be detected in compound VI. This coupling is efficient ($^5J_{H_5H_X}$ = 0.55 Hz). It is transmitted primarily through the σ-system via a planar zigzag-type fragment [3, 21], i.e., only in the s-cis($N_{(1)}$)-conformer of VI (structure E). For a fixed s-cis form the analogous SSCC would be equal to 0.75 Hz [3]. In the s-trans-conformation, on the other hand, the fragment separating the $H_{(5)}$ and H_X protons is not conducive to transmission of this long-range SSC, and the corresponding $^5J_{H_5H_X}$ SSCC value for the s-trans-form can be assumed to be equal to zero [21].



E

The conformer ratio in compound VI can therefore be expressed in the following way:

$$n_{trans} = \frac{^5J_{cis} - {}^5J_{obs}}{^5J_{cis} - {}^5J_{trans}} = \frac{0.20}{0.75} = 0.27, \tag{5}$$

where $^5J_{obs}$ is the value of the $^5J_{H_5H_X}$ SSCC in compound VI, and $^5J_{cis}$ and $^5J_{trans}$ are the SSCC values inferred for the s-cis and s-trans-forms, respectively. 2-Vinyltetrazole VI is characterized, therefore, by a slight preponderance of the s-cis-conformation.

Since the value of ΔJ reflecting the conformer populations in compounds VI-XI does not undergo significant changes (remaining in the range 1.8-2.0 Hz, with the exception of compound XI), it is assumed that a similar ratio of s-cis- and s-trans-conformers holds for all of the 2-vinyltetrazole derivatives.

EXPERIMENTAL

^{1}H-NMR spectra were recorded on a Tesla BS-567A (100 MHz) spectrometer, while ^{13}C-NMR spectra, and its proton coupled spectra, were obtained on a Bruker WP-200SY spectrometer (at 50.33 MHz). The values of the ^{13}C–^{1}H SSCC for the vinyl group were obtained based on analysis of the four-spin ABXZ system (Z = ^{13}C) for the β-isotopomer, and of the five-spin ABXMZ (Z = ^{13}C, M = 5-H) system for the α-isotopomer (in the case of 1-vinyltetrazole); the PANIC program run on an Aspect-2000 minicomputer was used for these analyses. The solvent was $CDCl_3$; HMDS was used as the internal standard. The sample concentrations were 5% for ^{1}H-NMR spectra, 30% for ^{13}C-NMR spectra. All of 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, V. K. Voronov, B. V. Trzhtsinskaya, E. V. Rudakova, and V. V. Keiko, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1264 (1987).
4. L. I. Vereshchagin, S. R. Buzilova, T. K. Mityukova, A. G. Proidakov, V. N. Kizhnyaev, V. V. Il'ina, G. T. Sukhanov, G. A. Gareev, and A. K. Bogens, Zh. Org. Khim., 22, 1979 (1986).
5. G. Levy and G. Nelson, Handbook of Carbon-13 Nuclear Magnetic Resonance [Russian translation], Mir, Moscow (1975), p. 86.
6. B. A. Trofimov, Heteroatomic Derivatives of Acetylene [in Russian], Nauka, Moscow (1981), p. 264.
7. O. A. Ivashkevich, P. N. Gaponik, and V. N. Naumenko, Khim. Geterotsikl. Soedin., No. 2, 236 (1987).
8. A. V. Afonin, V. K. Voronov, M. A. Andriyankov, and D. K. Danovich, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 317 (1987).
9. R. Knorr, Tetrahedron, 37, 929 (1981).
10. G. K. Hamer, J. R. Peat, and W. F. Reynolds, Can. J. Chem., 51, 897 (1973).
11. W. F. Reynolds, J. R. Peat, and G. K. Hamer, Can. J. Chem., 52, 3415 (1974).
12. A. R. Engelmann and R. H. Contreras, J. Quant. Chem., 23, 1033 (1983).
13. P. C. Myhre, J. W. Edmonds, and J. D. Kruger, J. Am. Chem. Soc., 88, 2459 (1966).
14. 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).
15. A. V. Afonin, V. K. Voronov, and M. A. Andriyankov, Khim. Geterotsikl. Soedin., No. 11, 1568 (1986).
16. S. Castellano, H. Gunther, and S. Ebersole, J. Phys. Chem., 69, 4166 (1965).
17. A. P. Ebdon, T. N. Huckerly, and F. G. Thorpe, Tetrahedron Lett., No. 31, 2921 (1971).
18. C. Li and M. P. Sammes, J. Chem. Soc., Perkin I, No. 9, 2193 (1983).
19. T. M. Spootswood and C. J. Tanzer, Aust. J. Chem., 20, 1277 (1967).
20. B. A. Trofimov, M. V. Sigalov, V. M. Bzhezovskii, G. A. Kalabin, S. E. Korostova, A. I. Mikhaleva, and L. A. Balabanova, Khim. Geterotsikl. Soedin., No. 6, 768 (1978).
21. T. Schaefer, G. H. Penner, K. J. Davie, and R. Sebastian, Can. J. Chem., 63, 777 (1985).