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QUANTUM-CHEMICAL INVESTIGATION OF THE ELECTRONIC AND SPATIAL STRUCTURE OF 1-VINYLTETRAZOLES

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*Calculations have been carried out of the total Mulliken charges on carbon and nitrogen atoms, the relative stability, and equilibrium populations of the s-cis(R) and s-trans(R) conformers of a series of 1-vinyl-5R-tetrazoles (R = H, Me, n-Bu, tert-Bu, Ph, NH_2, I, CF_3, NO_2) by the ab initio MP2/6-31G** method. Out-of-plane structures correspond to the stable s-cis(R) conformer, and the deviation from planarity grows regularly with an increase in the bulk of the substituent. The proportion of s-trans(R) conformation increases in the same series and reaches 100% for R = tert-C_4H_9. The data of quantum-chemical calculations are in agreement with the results of investigations of the spatial structure of 1-vinyl-5R-tetrazoles by ^1H and ^{13}C NMR methods. Values of the total energies of the corresponding homodesmotic reactions were calculated to assess the effect of the nature of the substituent in position 5 of the tetrazole ring on the size of the conjugation energy in planar s-trans(R) conformations of the compounds investigated. The quantum-chemical calculations carried out show that the conjugation energy decreases regularly according to the increase in electron-withdrawing properties of the substituent in position 5 of the ring.*

Keywords: 1-vinyltetrazoles, internal rotation, quantum-chemical calculations, ^1H and ^{13}C NMR spectra, conjugation energy.

Previously [1, 2] we carried out a quantum-chemical and spectroscopic investigation of the electronic structure and rotational isomerism of 2-vinyltetrazoles and 2-substituted 5-vinyltetrazoles, which are of interest for obtaining polymeric materials used in various highly effective combustible and thermally destroyable systems, compositions for generating gases, ultrafiltration membranes, and for a series of other purposes [3-6]. Results are given in the present work of an investigation of the effect of the nature of the substituent in position 5 of the ring on the spatial structure, charge distribution, energy of internal rotation, and the conjugation energy in 1-vinyltetrazole molecules (Scheme 1).

The phenomenon of rotational isomerism for N-vinyltetrazoles was investigated by ^1H and ^{13}C NMR methods. Attempts were undertaken, on the basis of the chemical shifts of the vinyl group protons and the direct J_{CH} coupling constants in the vinyl group, to assess the ratio of *s-cis* and *s-trans* conformers in solution [7]. However the series of monomers represented in [7], including only 5 compounds for 1-vinyltetrazoles, does not permit a systematic investigation of the effect of the nature of the substituent at the ring carbon atom on the spatial structure of the molecules, and on features of the conjugation between the electronic systems of the heterocycle and the vinyl group.

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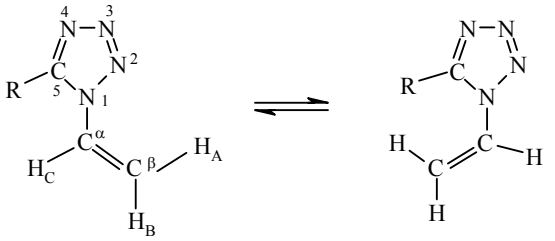
Scheme 1



s-trans(R) conformer *s-cis*(R) conformer

1 R = H, **2** R = Me, **3** R = *n*-Bu, **4** R = *t*-Bu, **5** R = Ph, **6** R = NH_2, **7** R = I, **8** R = CF_3, **9** R = NO_2

Calculations were carried out by the nonempirical methods MP2/6-31G* and MP2/6-31G**, which permit a fairly correct investigation of the energy characteristics and spatial structure of the tetrazole derivatives [1, 2, 8]. In the first stage the dependence was studied of the total energy and certain geometric parameters on the dihedral angle φ_1 between the vinyl group and and the plane of the tetrazole ring in the molecule of unsubstituted 1-vinyl-5H-tetrazole (**1**). The dihedral angles φ_1 and φ_2 and the direction of rotation of the substituents relative to the plane of the tetrazole ring in the molecules of 5-substituted 1-vinyltetrazoles are shown in Fig. 1.

Calculated energy profiles are given in Fig. 2, and the total Mulliken charges on atoms, the relative total energies, and certain geometric parameters of the structures corresponding to the minima on the curves of Fig. 2 are given in Table 1. As in the case of 2-substituted 5-vinyltetrazoles [1] the minima correspond to the planar *s-cis*(R) and *s-trans*(R) conformers, when the most favorable conditions for conjugation between the vinyl group and the tetrazole ring are achieved (Fig. 2). The maxima correspond to structures with $\varphi_1 = 90°$, in which there is no conjugation. It should be mentioned that in the region of values of the dihedral angle $\varphi_1 = 150\text{-}210°$ the total energy of the molecule changes to a significantly smaller degree than was observed for the 2- and 5-vinyltetrazoles investigated previously [1, 2].

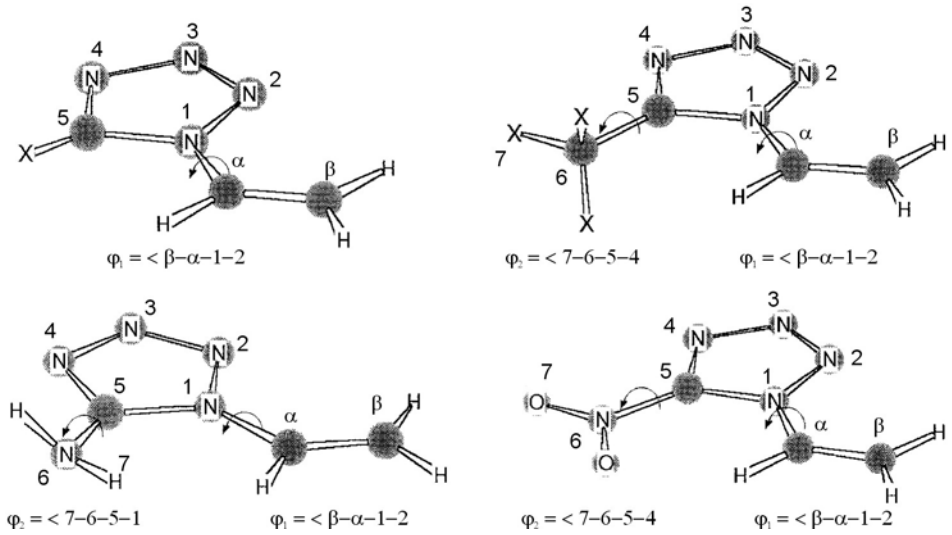


Fig. 1. Dihedral angles φ_1 and φ_2 and the direction of rotation of the substituent relative to the plane of the tetrazole ring in 1-vinyl-5R-tetrazole molecules.

TABLE 1. Total Mulliken Charges on the Carbon Atoms of the Vinyl Group and on the Ring Nitrogen Atoms, Bond Lengths C_α–$N_{(1)}$ and C_β–C_α, Valence Angle $\theta(C_\beta C_\alpha N_{(1)})$, Dipole Moment ($\mu$), Relative Energy ΔE and Proportion of *s-trans*-(R) Conformation n_{trans} for 1-Vinyl-5R-tetrazoles Calculated by the MP2/6-31G** Method

Compound	φ_1, deg	φ_2, deg	Total charges						Bond lengths, Å		$\theta(C_\beta C_\alpha N_{(1)})$, deg.	μ, D	ΔE, kJ/mole	n_{trans}, %
			$N_{(1)}$	$N_{(2)}$	$N_{(3)}$	$N_{(4)}$	C_α	C_β	C_α–$N_{(1)}$	C_β–C_α				
1	-0.5	—	-0.336	-0.048	-0.086	-0.291	0.117	-0.264	1.4167	1.3339	122.8	5.67	0.0	59.0
	179.5	—	-0.354	-0.046	-0.090	-0.286	0.139	-0.276	1.4146	1.3344	124.0	5.78	0.9	
2	0.0	0.0	-0.384	-0.045	-0.093	-0.322	0.117	-0.265	1.4150	1.3346	123.0	5.88	0.0	76.3
	160.0	12.3	-0.400	-0.045	-0.096	-0.316	0.133	-0.274	1.4142	1.3356	124.9	6.00	2.9	
4	23.8	-4.9	-0.408	-0.045	-0.096	-0.332	0.115	-0.258	1.4191	1.3351	122.0	5.70	0.0	100.0
6	16.1	66.5	-0.390	-0.044	-0.095	-0.346	0.107	-0.265	1.4130	1.3344	122.7	5.73	0.0	45.0
	157.6	-48.7	-0.416	-0.042	-0.098	-0.348	0.129	-0.295	1.4121	1.3366	123.8	6.12	-0.5	
7	0.0	—	-0.339	-0.036	-0.077	-0.270	0.118	-0.265	1.4181	1.3343	122.4	5.27	0.0	95.2
	137.7	—	-0.346	-0.037	-0.081	-0.262	0.117	-0.248	1.4214	1.3339	122.8	5.64	7.4	
8	12.5	3.3	-0.400	-0.029	-0.075	-0.300	0.110	-0.259	1.4215	1.3336	121.9	4.67	0.0	86.5
	148.4	12.3	-0.406	-0.029	-0.077	-0.293	0.124	-0.269	1.4233	1.3333	123.6	4.87	4.6	
9	15.3	-22.7	-0.394	-0.026	-0.063	-0.282	0.100	-0.256	1.4264	1.3342	120.9	4.67	0.0	98.7
	140.9	-44.9	-0.389	-0.024	-0.069	-0.277	0.130	-0.251	1.4232	1.3327	122.3	4.83	10.8	

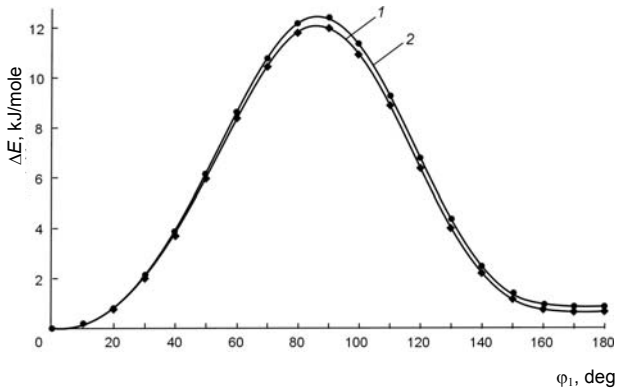


Fig. 2. Calculated dependencies of the relative total energy of the 1-vinyl-5H-tetrazole molecule on the dihedral angle φ_1 between the planes of the vinyl group (1) and the tetrazole ring (2).

The shape of the energy profile is probably caused by the fact that the gain in conjugation energy due to the change to a planar conformation is compensated by the steric repulsion between the H_A atom of the vinyl group and the hydrogen atom on the ring carbon atom. This hypothesis is confirmed by the sharp increase in valence angle $\theta(C_\beta C_\alpha N_{(1)})$ on changing φ_1 from 120 to 180° (Fig. 3, *c*).

Both planar conformations of 1-vinyl-5H-tetrazole have similar values of energy. The addition of polarizing *p*-functions for the hydrogen atoms therefore proved to have no significant effect on the shape of the energy profile (see Fig. 2). The equilibrium proportion of the *s-trans*(H) conformation of 1-vinyl-5H-tetrazole, calculated according to [10] from the difference in calculated total energies of the *cis* and *trans* conformers, was 59% (Table 1), which is in good agreement with the value found in [7] by analyzing the direct ^{13}C-^{1}H coupling constants in the vinyl group (62%).

However this agreement is probably fortuitous since on estimating the proportion of *s-trans*(R) conformation of 1-vinyl-5H-tetrazole the authors of [7] proceeded from the hypothesis that 5-methyl-1-vinyl-tetrazole exists exclusively in the *s-trans*(R) conformation, which is not in agreement with the results of the present work (Table 1). Nonetheless we note that the same good agreement between calculated and experimental data was obtained for 2-vinyltetrazole [2], the experimental proportion of the *s-trans*($N_{(1)}$) conformation of which was estimated by other criteria [7].

The dependencies of the bond lengths of C_α–$N_{(1)}$, C_β–C_α and the valence angle $\theta(C\beta\alpha N_{(1)})$ in the 1-vinyl-5H-tetrazole molecule on the dihedral angle φ_1 (relative to the geometric parameters of the *s-trans*(R) conformer) are given in Fig. 3. On going from the *s-trans*(R) conformation of 1-vinyl-5H-tetrazole ($\varphi_1 = 180°$) to a conformation with $\varphi_1 = 90°$ the C_α-$N_{(1)}$ bond length increases by 0.014 Å (Fig. 3, *a*). Approximately the same change was observed in the bond lengths of C_α–C_{ring} and C_α–$N_{(2)}$ in the molecules of 2-substituted 5-vinyltetrazoles and 2-vinyltetrazoles [1, 2]. The C_β–C_α bond length changes to a significantly lesser extent and reaches a minimum at $\varphi_1 = 90°$ (Fig. 3, *b*). The maximum value of the valence angle $\theta(C_\beta C_\alpha N_{(1)})$ corresponds to a planar conformation, which is probably linked with the highest steric repulsion (Fig. 3, *c*).

Analysis of the dependence of the enthalpy of formation (method AM1) and the total energy (method MP2/6-31G*) on the dihedral angles φ_1 and φ_2 in the 5-methyl-1-vinyltetrazole molecule shows that, unlike previously investigated vinyltetrazoles [1, 2], it is impossible to consider the rotation of the substituents relative to the plane of the ring in 1-vinyl-5R-tetrazoles as independent of one from the other. Consequently the investigation of the spatial structure of 1-vinyl-5R-tetrazoles must include calculation of the energies of the molecules as a function of the simultaneous rotation of the vinyl group and of the substituent relative to the plane of the ring.

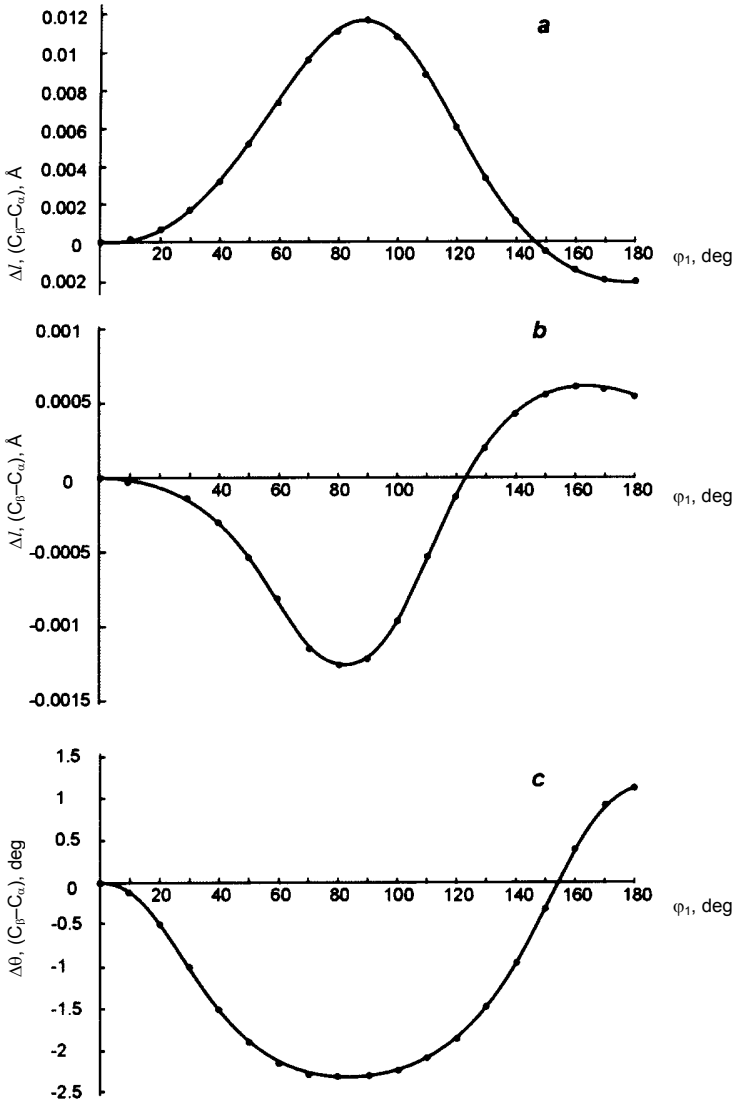


Fig. 3. Changes in the geometric parameters of the 1-vinyl-5H-tetrazole molecule as a function of the dihedral angle φ_1 between the planes of the vinyl group and the tetrazole ring, *a*) bond length C_α–$N_{(1)}$, *b*) bond length C_β–C_α, *c*) valence angle $\theta(C_\beta C_\alpha N_{(1)})$.

The data obtained indicate that the planar *s-cis*(R) conformation of 5-methyl-1-vinyltetrazole corresponds to a saddle point on the potential energy surface (PES) and a nonplanar *s-cis*(R) form to the minimum. The potential barrier to the *cis-cis* transition calculated by the MP2/6-31G** method is 0.37 kJ/mole, i.e. significantly lower than the value of *RT* at room temperature, and approximately equal to the zero vibration energy, calculated in an harmonic oscillator approach, corresponding to internal rotation around the C_α–$N_{(1)}$ bond. If one takes into account that the similar vibration must have a high degree of anharmonism, the problem even at low temperatures of the possibility of localization of the nuclear configuration of the *s-cis*(R) conformation of the 5-methyl-1-vinyltetrazole molecule in regions corresponding to the nonplanar minimum, remains not entirely clear.

Calculations by the AM1 and MP2/6-31G* methods gave qualitatively the same shape for the PES of 5-methyl-1-vinyltetrazole. Consequently, with the aim of investigating the spatial structure of the remaining 1-vinyltetrazoles **3**-**9**, we carried out calculations of the enthalpies of formation for them in relation to the dihedral angles φ_1 and φ_2 by the AM1 method. The optimized structures found in this way were used as a basis for carrying out nonempirical calculations.

Optimization of the geometry by the MP2/6-31G** method starting from the structures of the *s-trans*(R) conformers, obtained by the semiempirical AM1 method, also leads to a planar *s-trans*(R) conformer, except for 5-amino-1-vinyltetrazole **6**. However for the planar *s-trans*(R) conformations of the 5-*tert*-butyl-1-vinyl- and 5-trifluoromethyl-1-vinyltetrazole molecules there was one negative characteristic value in the force constant matrices, corresponding to rotation of the vinyl group relative to the plane of the tetrazole ring, and for the planar conformation of the *s-trans*(R)-5-nitro-1-vinyltetrazole molecule there were two negative characteristic values corresponding to the analogous rotation of the vinyl and nitro groups.

Taking this into account we carried out a repeat optimization of the geometry of the indicated 1-vinyltetrazoles by the MP2/6-31G** method starting from nonplanar starting structures. In this case this led to structures in which the vinyl group does not lie in the plane of the tetrazole ring (φ_1 = 12-15°). Calculation of the force constant matrices for them showed that these structures correspond to a minimum on the PES. Total energies for the nonplanar *s-trans*(R) conformations of the molecules of 5-*tert*-butyl-1-vinyl-, 5-trifluoromethyl-1-vinyl-, and 5-nitro-1-vinyltetrazole were lower than the corresponding values for the planar conformers by 0.48, 0.08, and 0.55 kJ/mole respectively. The nonempirical methods, unlike the AM1 method, predicted only one stable *s-cis*(R) conformation for 5-amino-1-vinyltetrazole.

Relative total energies, Mulliken charges on the carbon and nitrogen atoms, and certain geometric characteristics for conformations of the 1-vinyl-5R-tetrazoles, which correspond to minima on the PES, are shown in Table 1. Stable *s-cis*(R) conformations are nonplanar structures for the 1-vinyltetrazoles investigated. The deviation from planarity grows regularly with the increase in bulk of the substituent. According to the MP2/6-31G** calculation, dihedral angles φ_1 = 180° (**1**), φ_1 = 160° (**2**), φ_1 = 158° (**6**), φ_1 = 148° (**8**), φ_1 = 138-141° (**7**, **9**) correspond to the *s-cis*(R) conformation.

The proportion of the *s-trans*(R) conformation increases in the same series, and it is the sole stable conformation for 5-*tert*-butyl-1-vinyltetrazole. The exception is 5-amino-1-vinyltetrazole, which is characterized by a minimal content of *s-trans*(R) conformation in the series being considered (Table 1).

Data on the effect of the substituent in position 5 on conformational equilibrium obtained in quantum-chemical calculations are in agreement with the results of investigations of the spatial structure of 1-vinyl-5R-tetrazoles by ^{1}H and ^{13}C NMR methods. It is known [7, 10] that the differences in coupling constants $\Delta J = {}^1J_{C_\beta H_B} - {}^1J_{C_\beta H_A}$ in the ^{13}C NMR spectra and the chemical shifts of the terminal protons of vinyl groups $\Delta\delta = \delta_{H_A} - \delta_{H_B}$ may be used as parameters characterizing the conformational state of N-vinylazoles. This is due to the spatial proximity of the C_β–H_A bond and of the H_A proton to the unshared electron pair of atom $N_{(2)}$ (see Scheme 1) arising in the *s-trans*(R) conformation, and leads correspondingly to an additional contribution to the ${}^1J_{C_\beta H_A}$ coupling constant in comparison with ${}^1J_{C_\beta H_B}$ and an additional low field displacement of the chemical shift of the H_A proton [11, 12].

From the data given in Tables 1 and 2 it is seen that the parameters ΔJ and $\Delta\delta$ fall regularly according to the extent of the increase in the proportion of *s-trans*(R) conformation in the investigated series of 1-vinyltetrazoles. The exception is 5-amino-1-vinyltetrazole. In solutions and melts 1-substituted 5-aminotetrazoles are able to form various isomeric forms, including imino forms [13], consequently it may be suggested that the significant differences in J_{CH} coupling constant values and chemical shifts of the vinyl group protons for 5-amino-1-vinyltetrazole compared with the remaining compounds (Table 2) are linked with the presence of the iminotetrazoline form **6a** (Scheme 2).

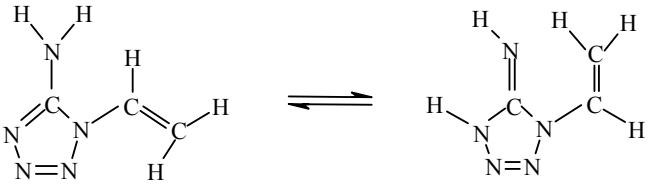
TABLE 2. ^{13}C and ^{1}H NMR Spectra of 1-Vinyl-5R-tetrazoles in Deuterochloroform

Compound	Chemical shifts in ^{13}C NMR spectra, δ, ppm			Coupling constants in ^{13}C NMR spectra (J, Hz)							Chemical shifts in ^{1}H NMR spectra, δ, ppm				J Constants in ^{1}H NMR spectra (Hz)		
	C_{ring}	C_α	C_β	$^{1}J_{C_\beta H_A}$	$^{1}J_{C_\beta H_B}$	ΔJ	$^{1}J_{C_\alpha H_C}$	$^{2}J_{C_\beta H_C}$	$^{2}J_{C_\alpha H_B}$	$^{2}J_{C_\alpha H_A}$	H_A	H_B	Δδ	H_C	$^{2}J_{H_A H_B}$	$^{3}J_{H_A H_C}$	$^{3}J_{H_B H_C}$
1	140.74	125.97	108.50	161.8	166.2	4.4	188.6	2.6	4.0	7.0	6.00	5.41	0.59	7.36	-2.1	15.8	8.9
2	149.85	124.94	108.90	162.5	165.7	3.2	185.7	2.6	4.3	6.9	6.04	5.43	0.61	7.06	-1.5	15.4	8.7
3	153.64	125.07	109.87	162.9	165.5	2.6	184.6	2.0	4.0	6.9	6.07	5.40	0.67	7.02	-1.3	15.4	8.8
5	164.83	129.79	108.40	163.1	166.0	2.9	187.4	2.5	4.2	7.1	6.17	5.38	0.79	7.07	-1.4	15.2	8.7
6*	155.53	126.21	106.90	159.8	163.9	4.1	182.2	1.8	4.3	6.5	5.83	5.35	0.48	6.89	-1.6		
7	103.20	126.36	111.86	163.5	165.2	1.7	187.0	2.3	4.5	7.0	6.14	5.53	0.61	7.23	-1.3	15.4	
8*[2]	—	—	114.41	163.9	166.6	2.7	190.3	—	—	—	6.31	5.68	0.63	7.21	-2.05	—	8.8

* Solution in deuteromethanol.

*[2] Data of [7].

Scheme 2



6 **6a**

To assess the relative stability of the **6** and **6a** molecules we have carried out calculations by the MP2/6-31G** method of the total energies of all the possible conformations of 5-amino-4H-1-vinyltetrazoline. The data obtained show that the energetically most stable conformation of the **6a** molecule, illustrated in Scheme 2, is 53 kJ/mole less stable than the amino form. Estimated from the difference in total energy the equilibrium content of the imino form is only 5×10^{-8} %. The carried out calculations therefore show that the anomalously low values of certain parameters of the NMR spectra for 5-amino-1-vinyltetrazole are not linked with the possibility of isomerization reactions taking place in solution, and are probably caused by a specific effect of the amino group creating an asymmetric intramolecular electric field [14, 15].

Data on the electron density distribution show that, unlike the 5-substituted 2-vinyltetrazoles investigated previously, the charges on the carbon atoms of the vinyl group in 1-vinyl-5R-tetrazoles are changed significantly on going from the *s-trans*(R) to the *s-cis*(R) conformer. The electron density on the β-carbon atom for *s-trans*(R) conformers falls regularly on introducing electron-withdrawing substituents. Consequently when comparing the values of charges on atoms with the data on chemical shift δ_{C_β} in the ^{13}C NMR spectra of the 1-vinyltetrazoles investigated, it is necessary to consider the relative content of conformers. Thus the charges on the C_β atom in the *s-trans*(R) conformations of the 1-vinyltetrazole molecules **2** and **6** are practically identical. However in the case of compound **6** the predominating conformation is *s-cis*(R), in which the electron density on the β-carbon atom is significantly greater than in the *s-trans*(R) conformation (Table 1). Probably the displacement of the signal of the C_β atom in the ^{13}C NMR spectrum of 5-amino-1-vinyltetrazole **6** into the high field region may be explained by this.

The height of the barrier to internal rotation in systems with conjugated bonds depends, apart from the conjugation energy, on such factors as steric interactions, hyperconjugation effects, etc. However in the case of the investigated 2-vinyl-tetrazoles and 2-substituted 5-vinyltetrazoles, in the molecules of which the substituent in the ring and the vinyl group are sterically separated, the influence of steric effects is insignificant compared with the electronic effects, and for the indicated series of vinyltetrazoles the height of the barrier correlates at the qualitative level with the conjugation energy [1, 2]. The data obtained indicate that for 1-vinyl-5R-tetrazoles, by virtue of the spatial proximity of the vinyl group and the substituent, the change in the height of the barrier to internal rotation may not characterize the change in conjugation energy between the vinyl group and the tetrazole ring.

In the present work the total energy of the corresponding homodesmotic reaction was used as a figure characterizing the change in conjugation energy in the planar *s-trans*(R) conformation of the investigated 1-vinyl-5R-tetrazoles in comparison with the *s-trans*(H) conformation of unsubstituted 1-vinyltetrazole [16] (Scheme 3).

Scheme 3

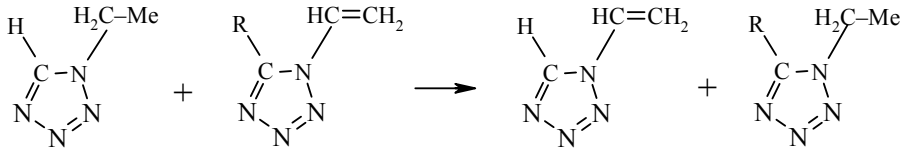


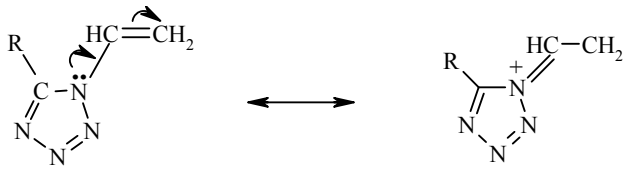
TABLE 3. Relative Reaction Energies ($\Delta_r E$) (Scheme 3) and Dihedral Angles φ_1 and φ_2 (Fig. 1) in 1-Ethyl-5R-tetrazole Molecules Calculated by the MP2/6-31G** Method

R	φ_1, deg.	φ_2, deg.	$\Delta_r E$, kJ/mol
H	71.4	—	—
CH_3	80.2	-0.9	1.1
t-C_4H_9	74.1	-6.9	0.3
NH_2	83.0	68.8	1.6
I	86.9	—	-2.4
CF_3	82.5	-3.1	-5.4
NO_2	92.0	13.8	-8.7

The calculated geometric characteristics of 1-ethyl-5R-tetrazoles and the relative reaction energies are given in Table 3. In the stable conformations of all the 1-ethyl-5R-tetrazoles investigated the ethyl group does not lie in the plane of the tetrazole ring ($\varphi_1 \sim 70$-$90°$), which leads to a reduction in the steric repulsion between the methyl group and the $N_{(2)}$ nitrogen atom of the tetrazole ring. The obtained data show that the total energy of the reaction is reduced on going from an electron-donating to an electron-withdrawing substituent.

It is possible to explain qualitatively a similar relationship starting from simple valence bond theory, according to which it is possible to employ resonance of the two canonical structures to describe the C_α–$N_{(1)}$ and C_β–C_α chemical bonds in 1-vinyltetrazole molecules (Scheme 4). Such a consideration enables 1-vinyltetrazoles to be formally assigned as enamines [17], in the molecules of which conjugation of the unshared electron pair on the nitrogen atom with the π-system of the vinyl group leads to the generation of a negative charge on its terminal carbon atom.

Scheme 4



It is evident that electron-donating substituents will stabilize and electron-withdrawing substituents will destabilize a structure with divided charges. This statement is in agreement with the change in electron density on the C_β carbon atom and the length of the C_α–$N_{(1)}$ bond on going from electron-donating to electron-withdrawing substituents (Table 1).

The data obtained indicate that, unlike 2-vinyltetrazoles [2], the nature of the substituent in position 5 of the ring proves to have a significant effect on the electronic structure, the conformational state, the energy for internal rotation, and conjugation in 1-vinyl-5R-tetrazole molecules, among which the special features of homo- and copolymerization and the properties of polymers have been studied in fair detail only for 1-vinyltetrazole and 5-methyl-1-vinyltetrazole [18]. The data on the electronic structure and conjugation energies in 1-vinyltetrazole molecules may be used for predicting their reactivity in (co)polymerization processes by various mechanisms. However it is necessary to consider the inclination of 1- and 1,5-substituted tetrazole molecules to associate and solvate specifically [19], which must be displayed in a different way for 1-vinyl-5R-tetrazoles with substituents of various nature.

EXPERIMENTAL

The quantum-chemical calculations were carried out using GAMESS 99 and MOPAC 7 sets of programs. When investigating the relationships of energies and geometric parameters to the dihedral angles φ_1 and φ_2, characterizing the rotation of the vinyl (ethyl) group and the substituent, these angles were changed with a step of 10°, and all the remaining internal coordinates were optimized (in the case of 5-amino-1-vinyltetrazole the dihedral angle between the planes and the hydrogen atoms of the amino group was fixed at 130°). Stable conformations of 1-vinyltetrazoles (1-ethyltetrazoles) were obtained by full optimization of their geometry without symmetry restrictions and were characterized with the aid of calculations of analytical force constant matrices. On carrying out nonempirical calculations for 5-iodo-1-vinyltetrazole (1-ethyl-5-iodotetrazole) the basis set 6-311G* was used for iodine atoms and basis set 6-31G** for all the remainder [20].

The ^{1}H and ^{13}C NMR spectra of 1-vinyltetrazoles were recorded in deuterochloroform on a Bruker WM-360 instrument (90 MHz for ^{13}C NMR spectra). Internal standard was HMDSO (δ 0.055 ppm relative to TMS). Solution concentrations were 0.5 (for ^{1}H NMR spectra) and 3.0 M (for ^{13}C NMR spectra).

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