

Tautomerism of 1,3,4-thiadiazole. Part II

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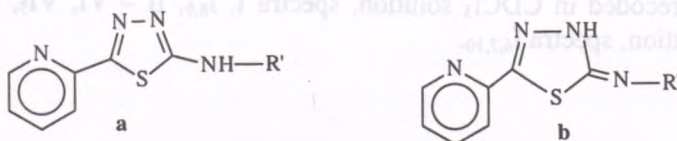
On the basis of the ^1H NMR spectra of 5-(2'-pyridyl)-2-allylamino-1,3,4-thiadiazole the presence of the tautomeric modifications **1a** **1b** **1c** has been stated. The chemical shifts values of the protons of allyl substituent indicate the sp^3 , sp^2 hybridization of exocyclic nitrogen atom 2N(5N) and the presence of the tautomeric modifications **1a** **1b** **1c** in both kinds of hybridization. The coupling constants of the protons of allyl substituent support the presence of the structures **1a_d**, **1b_d**, **1c_d**, **1a_e**, **1b_e**, **1c_e**, **1a_d** **1b_d** **1c_d**, **1a_e** **1b_e** **1c_e** as well as the transformation of the structures **1a_e** **1b_e** **1c_e** \Leftrightarrow **1a_d** **1b_d** **1c_d**, **1a_e** **1b_e** **1c_e** \Leftrightarrow **1a_d** **1b_d** **1c_d**. The long-range range coupling constants confirm the existence of the rigid structures **1a_e**, **1b_e**, **1c_e** and sp^2 hybridization of exocyclic nitrogen atom 2N(5N).

1. INTRODUCTION

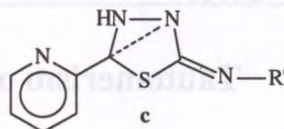
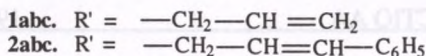
In the previous paper [1] it has been reported that in the ^1H NMR spectra of 5-(2'-pyridyl)-2-allyl-(cinnamyl)-amino-1,3,4-thiadiazole **1a**, **2a** (Scheme 1) the signals of NH group there are present in the range δ 13.64 - (-0.033).

It suggests the existence of the tautomeric modifications 3H-5(2'-pyridyl)-2-allyl-(cinnamyl)-imino-1,3,4-thiadiazole **1b**, **2b** and 3H-2(2'-pyridyl)-5-allyl-(cinnamyl)-imino-1,3,4-thiadiazole **1c**, **2c** as well as various mesomeric forms of these tautomeric structures **1abc**, **2abc**.

Scheme 1



Scheme 1 cont.



It has been earlier stated [1] that the signal of NH group in the range δ 13.64 – 3.562 point to the lack of the interactions of 2p orbitals of the nitrogen atoms 3N 4N of 1,3,4 – thiadiazole ring in the mesomeric modifications of the tautomeric forms **1abc**, **2abc**.

The exocyclic nitrogen atom 2N(5N) of 1,3,4 – thiadiazole ring of **1abc**, **2abc** tautomers may show $sp^3 sp^2$ and $sp^2 sp$ hybridization, respectively. Consequently **1abc**, **2abc** tautomers may appear in both kinds of hybridization, the structures **1a_{de}** **1b_{de}** **1c_{de}**, **2a_{fg}** **2b_{fg}** **2c_{fg}**, respectively and **1a_e** **1b_e** **1c_e**, **2a_{fg}** **2b_{fg}** **2c_{fg}** tautomers may exist as the mesoionic forms **1h** **1i** **1j**, **2h** **2i** **2j**, respectively [1].

The synthesis and some properties of mesoionic 1,3,4-thiadiazoles have been summarized by C.G. Newton and C.A. Ramsden [2,3].

The aim of the present paper has been to prove the presence of the tautomeric forms **1abc** (Scheme 1) in both kinds of hybridization sp^3 , sp^2 on the basis of the ¹H NMR spectra of product **1abc**.

The ¹H NMR spectra of product **1abc** obtained by the cyclization of N¹- (allylthiocarbamyl)- N³-phenyl-2-picolineamidrazone with ethanolic solution of HCl, diluted or concentrated hydrochloric acid at room or boiling temperature, methods I-IV [1]:

- I. diluted 3.6% ethanolic solution of HCl at room temperature
- II. diluted 3.6% hydrochloric acid at room temperature
- III. concentrated 36% hydrochloric acid at room temperature
- IV. boiling concentrated 36% hydrochloric acid

or by condensation of N³-phenyl-2-picolineamidrazone dihydrochloride and allylthiocarbamate in different solvents [1] methods V, VI:

- V. boiling anhydrous ethanol
- VI. boiling N,N-dimethylformamide

have been recoded in CDCl₃ solution, spectra I, I_{8,9}, II – VI, VI₃, VI₄ and in DMSO solution, spectra I_{6,7,10}.

The ^1H NMR spectra $I_{6,9}$ have been taken applying various concentration of product **1abc** obtained by method I in DMSO or CDCl_3 solutions:

- in a DMSO solution, the concentration of product **1abc** amounts to (1:3) spectra I_6 , I_7 , respectively
- in CDCl_3 solution, the concentration of product **1abc** amounts to: 10 mg/0.5 ccm spectrum I_8 , 25mg/ 0.5 ccm (maximal concentration) spectrum I_9

The ^1H NMR spectra I – VI, VI_3 , VI_4 [1] have been recorded in a CDCl_3 solution, I_{10} in a DMSO solution without any determination of the concentration of **1abc** product.

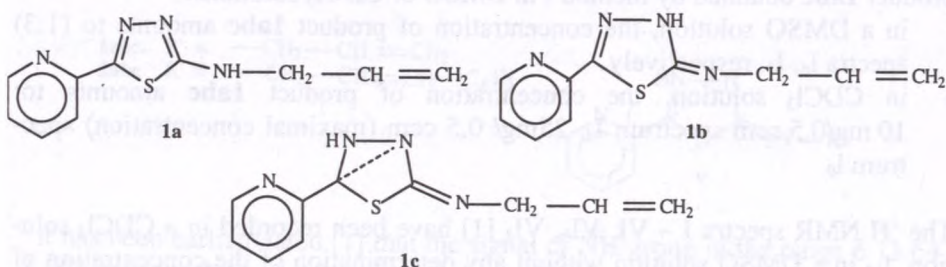
2. RESULTS AND DISCUSSION

In the ^1H NMR spectra I_6 , I_7 of products **1abc** in a DMSO solution, the signal of NH group appear at δ 8.270 (1.08H broaded triplet), δ 8.310 (1.05H degenerated, broaded triplet) respectively (Table 1). The broaded triplet suggests that these protons take part in the intermolecular hydrogen bonds. The presence of the broaded triplet in the ^1H NMR spectrum I_6 indicates the slow exchange of the proton of NH group, due to this fact, the coupling of the protons of $-\text{NH}-\text{CH}_2-$ group may be observed and support the existence of **1a** tautomer. The degenerated broaded triplet at δ 8.310 in the ^1H NMR spectrum I_7 support the existence of **1a 1b 1c** tautomers. These signals are the averaged ones in consequence of the rapid transitions of hydrogen atom between the exocyclic nitrogen atom 2N(5N) and 3N 4N ones of 1,3,4 – thiadiazole ring. These signals disappear in D_2O (spectrum I_{10}).

The chemical shifts and the coupling constants values of the protons of allyl substituent as well as the long-range coupling constants support the different hybridization sp^3 , sp^2 of exocyclic nitrogen atom 2N(5N) of **1a 1b 1c** tautomers.

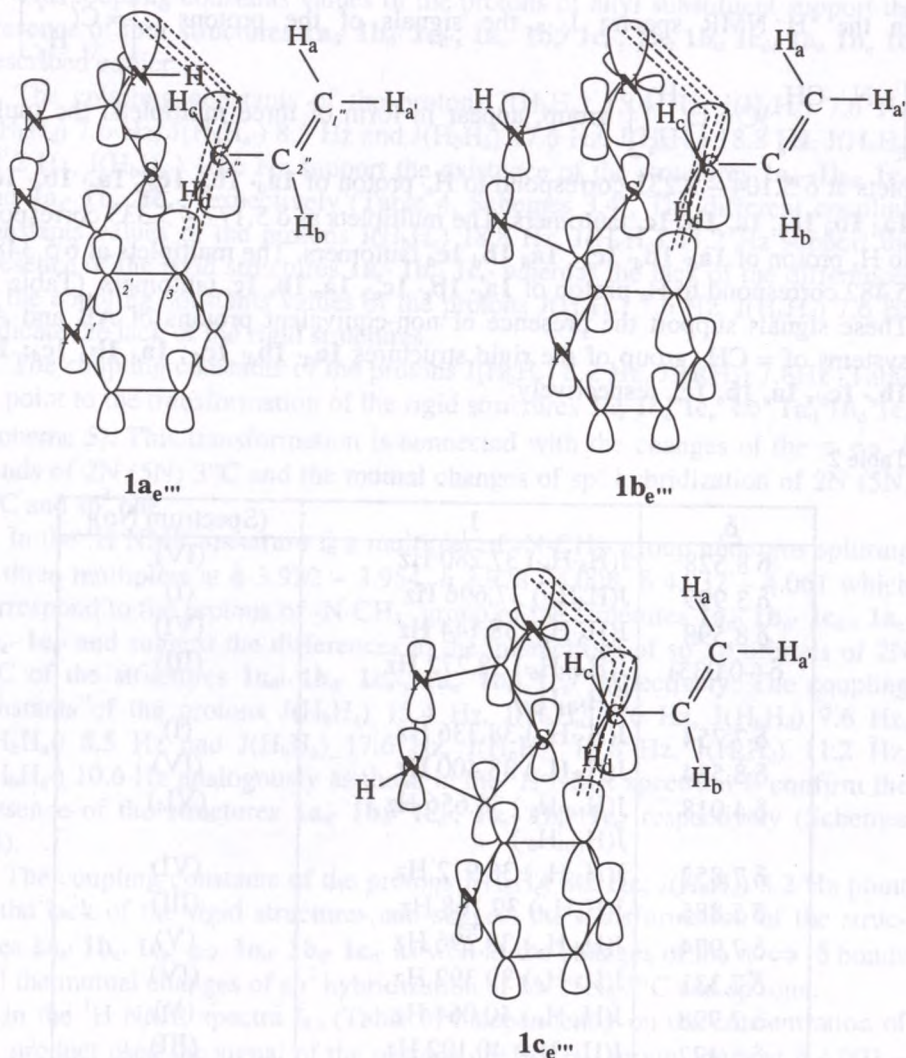
The long-range coupling constants of the protons in the range 37.280 Hz – 43.776 Hz spectra I – VI, VI_3 , VI_4 [1] (Table 2), support the presence of the coupling of the protons of the pyridyl and $-\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$ groups via 2p orbitals of $3'\text{C}$ $3''\text{C}$ of the rigid structures **1a_e**, **1b_e**, **1c_e** (Scheme 2) and indicate sp^2 hybridization of exocyclic nitrogen atom 2N(5N).

Table 1



NH			
Spectrum No (solvent)			
I ₆ (DMSO)	I ₇ (DMSO)	I ₈ (CDCl ₃)	I ₉ (CDCl ₃)
δ 8.637 - 8.562 0.08H	δ 8.665 - 8.589 -----	δ 8.606 - 8.530 0.2H	δ 8.601 - 8.525 0.05H
δ 8.325 - 8.213 1.08H	δ 8.355 - 8.267 1.05H	-----	-----
δ 8.135 - 7.988 0.17H	δ 8.174 - 8.010 -----	δ 8.245 - 8.145 0.28H	δ 8.237 - 8.137 0.05H
δ 7.935 - 7.837 0.25H	δ 7.954 - 7.859 0.05H	δ 7.859 - 7.688 0.35H	δ 7.854 - 7.681 0.16H
δ 7.503 - 7.336 0.08H	δ 7.517 - 7.381 -----	δ 7.349 - 7.212 0.6H	δ 7.342 - 7.205 0.16H
-----	-----	δ 6.221 - 6.207 1H s	δ 6.771 1H s
δ 6.148 - 5.772 -----	δ 6.187 - 5.809 0.05H	δ 6.160 - 5.782 0.5H	δ 6.160 - 5.782 0.1H
δ 5.399 - 5.104 0.33H	δ 5.435 - 5.133 0.05H	δ 5.482 - 5.191 0.7H	δ 5.482 - 5.184 0.2H
δ 4.061 - 3.922 0.25H	δ 4.086 - 3.988 0.05H	δ 4.086 - 4.003 0.53H	δ 4.086 - 4.003 0.2H

Scheme 2



In the ^1H NMR spectra $I_6 - I_{10}$ there occur two pairs of triplets of $=\text{CH}_b-$ group (Table 4) and indicate the existence of **1a** **1b** **1c** tautomers in both kinds of hybridization. The triplets at δ 5.997 – 6.033, δ 5.924 – 5.960 correspond to H_b proton of *Z* and *E* isomers, respectively of **1a_d**, **1b_d**, **1c_d**, **1a_d**, **1b_d**, **1c_d** tautomers in which the exocyclic nitrogen atom 2N(5N) shows sp^3 hybridization, the second pair of triplets at δ 6.097 – 6.133, δ 5.824 – 5.860 correspond to H_b proton of *Z* and *E* isomers, respectively of **1a_e**, **1b_e**, **1c_e**, **1a_e**, **1b_e**, **1c_e** tautomers with sp^2 hybridization of 2N(5N) (Schemes 3,4,5).

In the ^1H NMR spectra I_{6-10} the signals of the protons $\left[=\text{C} \begin{array}{l} \text{H}_a \\ \text{H}_{a'} \end{array} \right]$ of $\left[-\text{N}-\underset{\text{H}_b}{\text{CH}_2} \right] \text{C} = \text{C} \begin{array}{l} \text{H}_a \\ \text{H}_{a'} \end{array} \right]$ group, appear in form of three multiplets: the multiplets at δ 5.104 – 5.235 correspond to H_a proton of **1a_{d'}**, **1b_{d'}**, **1c_{d'}**, **1a_{e'}**, **1b_{e'}**, **1c_{e'}**, **1a_d**, **1b_d**, **1c_d**, **1a_e**, **1b_e**, **1c_e** tautomers. The multiplets at δ 5.177 – 5.333 correspond to H_a proton of **1a_{d'}**, **1b_{d'}**, **1c_{d'}**, **1a_d**, **1b_d**, **1c_d** tautomers. The multiplets at δ 5.348 – 5.482 correspond to H_a proton of **1a_{e'}**, **1b_{e'}**, **1c_{e'}**, **1a_e**, **1b_e**, **1c_e** tautomers, (Table 5). These signals support the presence of non-equivalent protons of AB and AX systems of $=\text{CH}_2$ group of the rigid structures **1a_{d'}**, **1b_{d'}**, **1c_{d'}**, **1a_d**, **1b_d**, **1c_d**; **1a_{e'}**, **1b_{e'}**, **1c_{e'}**, **1a_e**, **1b_e**, **1c_e**, respectively.

Table 2

δ ,	J,	(Spectrum No)
δ 8.528	$J(\text{H}_6, \text{H}_a)$ 37.280 Hz	(IV)
δ 3.999	$J(\text{H}_d \text{H}_6)$ 37.696 Hz	(I)
δ 8.598	$J(\text{H}_6, \text{H}_a)$ 38.144 Hz	(VI)
δ (-0.033)	$J(\text{H}_{\text{NH}} \text{H}_6)$ 38.272 Hz $J(\text{H}_{\text{NH}} \text{H}_a)$	(III)
δ 7.754	$J(\text{H}_5, \text{H}_a)$ 38.336 Hz	(I)
δ 8.584	$J(\text{H}_6, \text{H}_a)$ 38.400 Hz	(IV)
δ 4.018	$J(\text{H}_{\text{NH}} \text{H}_a)$ 38.656 Hz $J(\text{H}_{\text{NH}} \text{H}_6)$	(VI ₄)
δ 7.852	$J(\text{H}_5, \text{H}_a)$ 38.912 Hz	(VI)
δ 5.886	$J(\text{H}_b \text{H}_3)$ 39.168 Hz	(III)
δ 7.974	$J(\text{H}_4, \text{H}_a)$ 39.296 Hz	(V)
δ 7.331	$J(\text{H}_3, \text{H}_a)$ 39.392 Hz	(IV)
δ 7.998	$J(\text{H}_4, \text{H}_a)$ 40.064 Hz	(V)
δ 5.477	$J(\text{H}_a, \text{H}_4)$ 40.192 Hz	(III)
δ 7.341	$J(\text{H}_3, \text{H}_a)$ 40.640 Hz	(IV)
δ 8.152	$J(\text{H}_4, \text{H}_a)$ 40.672 Hz	(I)
δ 5.214	$J(\text{H}_a \text{H}_3)$ 43.712 Hz	(IV)
δ 8.223	$J(\text{H}_4, \text{H}_a)$ 43.776 Hz	(V)

In the ^1H NMR spectra $I_{7,10}$ a signal of $-\text{N}-\text{CH}_2-$ group arises as a multiplet at δ 3.988 – 4.086 (Table 3) and indicates the presence of the structures **1a_{d'}**, **1b_{d'}**, **1c_{d'}**, **1a_{e'}**, **1b_{e'}**, **1c_{e'}**, **1a_d**, **1b_d**, **1c_d**, **1a_e**, **1b_e**, **1c_e**, (Schemes 3,4,5).

The coupling constants values of the protons of allyl substituent support the presence of four structures **1a_d**, **1b_d**, **1c_d**, **1a_e**, **1b_e**, **1c_e**, **1a_d** **1b_d** **1c_d**, **1a_e** **1b_e** **1c_e** described earlier.

The coupling constants of the protons $J(\text{H}_b\text{H}_a)$ 15.4 Hz, $J(\text{H}_b\text{H}_c)$ 7.6 Hz, $J(\text{H}_b\text{H}_d)$ 7.6 Hz, $J(\text{H}_b\text{H}_{a'})$ 8.5 Hz and $J(\text{H}_b\text{H}_a)$ 17.6 Hz, $J(\text{H}_b\text{H}_c)$ 18.8 Hz, $J(\text{H}_b\text{H}_d)$ 11.2 Hz, $J(\text{H}_b\text{H}_{a'})$ 10.6 Hz support the existence of the structures **1a_d**, **1b_d**, **1c_d** and **1a_e**, **1b_e**, **1c_e**, respectively (Table 4, Schemes 3,4). The different coupling constants values of the protons $J(\text{H}_b\text{H}_c)$ 18.8 Hz, $J(\text{H}_b\text{H}_d)$ 11.2 Hz support the presence of the rigid structures **1a_e**, **1b_e**, **1c_e** whereas the lack of the differences in the coupling constants values of the protons $J(\text{H}_b\text{H}_c)$ 7.6 Hz, $J(\text{H}_b\text{H}_d)$ 7.6 Hz indicate the lack of the rigid structures.

The coupling constants of the protons $J(\text{H}_b\text{H}_c)$ 8.2 Hz, $J(\text{H}_b\text{H}_d)$ 7.8 Hz (Table 4) point to the transformation of the rigid structures **1a_e** **1b_e** **1c_e** \leftrightarrow **1a_d** **1b_d** **1c_d** (Scheme 5). This transformation is connected with the changes of the $\pi \leftrightarrow \delta$ bonds of 2N (5N) 3''C and the mutual changes of sp^2 hybridization of 2N (5N) 3''C and sp^3 one.

In the ^1H NMR spectrum I_6 a multiplet of -N-CH₂- group undergoes splitting to three multiplets at δ 3.922 – 3.954, δ 3.978 – 4.008, δ 4.032 – 4.061 which correspond to the protons of -N-CH₂- group of the structures **1a_d**, **1b_d**, **1c_d**, **1a_e**, **1b_e**, **1c_e** and suggest the differences in the interactions of sp^3 , p orbitals of 2N 3''C of the structures **1a_d**, **1b_d**, **1c_d**, **1a_e**, **1b_e**, **1c_e**, respectively. The coupling constants of the protons $J(\text{H}_b\text{H}_a)$ 15.4 Hz, $J(\text{H}_b\text{H}_c)$ 7.6 Hz, $J(\text{H}_b\text{H}_d)$ 7.6 Hz, $J(\text{H}_b\text{H}_{a'})$ 8.5 Hz and $J(\text{H}_b\text{H}_a)$ 17.6 Hz, $J(\text{H}_b\text{H}_c)$ 18.8 Hz, $J(\text{H}_b\text{H}_d)$ 11.2 Hz, $J(\text{H}_b\text{H}_{a'})$ 10.6 Hz analogously as those in the ^1H NMR spectrum I_7 confirm the presence of the structures **1a_d**, **1b_d**, **1c_d**, **1a_e**, **1b_e**, **1c_e**, respectively (Schemes 3,4).

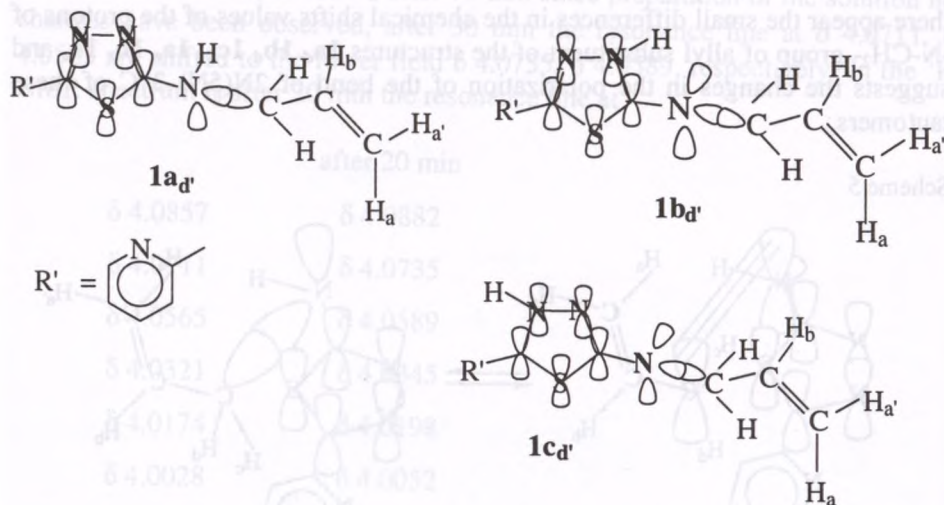
The coupling constants of the protons $J(\text{H}_b\text{H}_c)$ 8.2 Hz, $J(\text{H}_b\text{H}_d)$ 8.2 Hz point to the lack of the rigid structures and suggest the transformation of the structures **1a_e**, **1b_e**, **1c_e** \leftrightarrow **1a_d**, **1b_d**, **1c_d**, as well as the changes of the $\pi \leftrightarrow \delta$ bonds and the mutual changes of sp^2 hybridization of 2N (5N) 3''C and sp^3 one.

In the ^1H NMR spectra $I_{8,9}$ (Table 3) independently on the concentration of the product used the signal of the protons of -N-CH₂- group arises at δ 4.003 – 4.086 as two triplets δ 4.003 – 4.032, δ 4.056 – 4.086 and supports the presence of non-equivalent protons AB system of -N-CH₂- group of a rigid structures **1a_d** **1b_d** **1c_d**, **1a_e** **1b_e** **1c_e**, (Scheme 5).

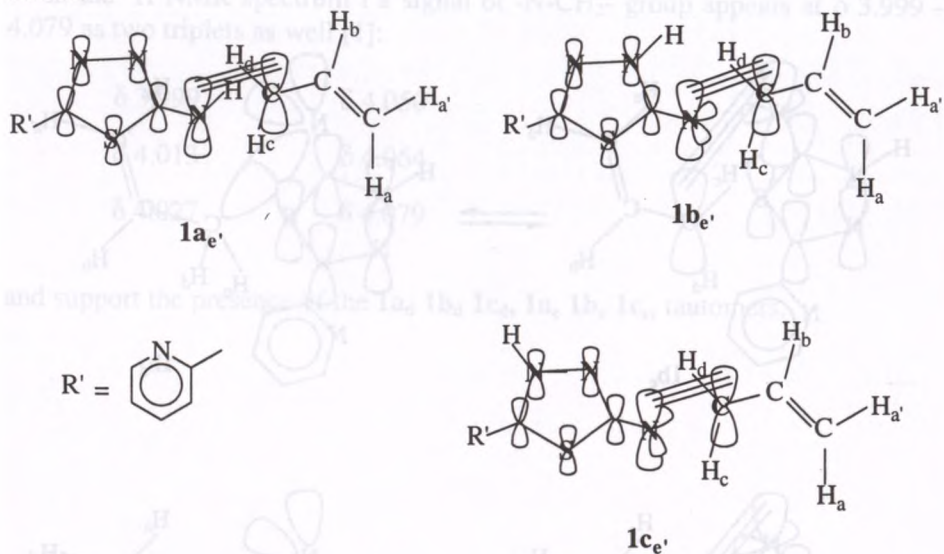
Table 3

Spectrum No (solvent)	=CH ₂	=CH-	-N-CH ₂ -	2'-pyridyl
I ₆ (DMSO)	δ 5.104 - 5.399 2H m	δ 5.772 - 6.148 1H m	δ 3.922 - 4.061 2H m	δ 8.637 - 8.562 1H α δ 8.135 - 7.988 1H γ δ 7.935 - 7.837 1H β δ 7.503 - 7.336 1H β
I ₇ (DMSO)	δ 5.133 - 5.435 2H m	δ 5.809 - 6.187 1H m	δ 3.988 - 4.086 2H m	δ 8.665 - 8.589 1H α δ 8.174 - 8.010 1H γ δ 7.954 - 7.859 1H β δ 7.517 - 7.381 1H β
I ₈ (CDCl ₃)	δ 5.191 - 5.482 2H m	δ 5.782 - 6.160 1H m	δ 4.003 - 4.086 2H m	δ 8.606 - 8.530 1H α δ 8.245 - 8.145 1H γ δ 7.859 - 7.688 1H β δ 7.349 - 7.212 1H β
I ₉ (CDCl ₃)	δ 5.184 - 5.482 2H m	δ 5.782 - 6.160 1H m	δ 4.003 - 4.086 2H m	δ 8.601 - 8.525 1H α δ 8.237 - 8.137 1H γ δ 7.854 - 7.681 1H β δ 7.342 - 7.205 1H β
I ₁₀ DMSO + D ₂ O	δ 5.143 - 5.431 2.21H m	δ 5.804 - 6.180 1.14H m	δ 4.069 - 3.988 2.5H m	δ 8.662 - 8.586 1.07H α δ 8.174 - 8.023 1H γ δ 7.967 - 7.869 1.42H β δ 7.532 - 7.395 1.21H β

Scheme 3



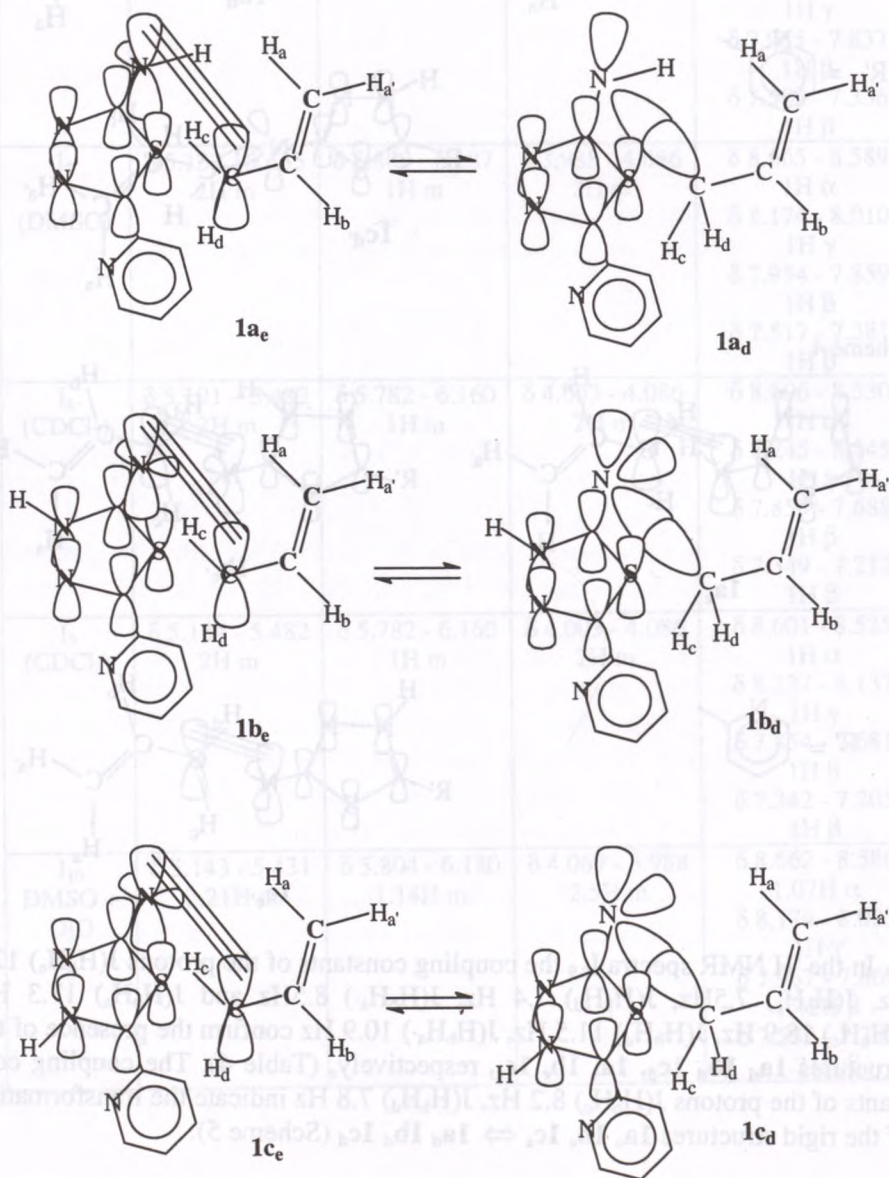
Scheme 4



In the ^1H NMR spectra $\text{I}_{8,9}$ the coupling constants of the protons $J(\text{H}_b\text{H}_a)$ 12.3 Hz, $J(\text{H}_b\text{H}_c)$ 7.5 Hz, $J(\text{H}_b\text{H}_d)$ 7.4 Hz, $J(\text{H}_b\text{H}_{a'})$ 8.5 Hz and $J(\text{H}_b\text{H}_a)$ 17.3 Hz, $J(\text{H}_b\text{H}_c)$ 18.9 Hz, $J(\text{H}_b\text{H}_d)$ 11.5 Hz, $J(\text{H}_b\text{H}_{a'})$ 10.9 Hz confirm the presence of the structures $\mathbf{1a}_d$ $\mathbf{1b}_d$ $\mathbf{1c}_d$, $\mathbf{1a}_e$ $\mathbf{1b}_e$ $\mathbf{1c}_e$, respectively, (Table 4). The coupling constants of the protons $J(\text{H}_b\text{H}_c)$ 8.2 Hz, $J(\text{H}_b\text{H}_d)$ 7.8 Hz indicate the transformation of the rigid structures $\mathbf{1a}_e$ $\mathbf{1b}_e$ $\mathbf{1c}_e \rightleftharpoons \mathbf{1a}_d$ $\mathbf{1b}_d$ $\mathbf{1c}_d$ (Scheme 5).

In the ^1H NMR spectra $I_{8,9}$ one can observe insignificant changes in time; there appear the small differences in the chemical shifts values of the protons of $-\text{N}-\text{CH}_2-$ group of allyl substituent of the structures **1a_d**, **1b_d**, **1c_d**, **1a_e**, **1b_e**, **1c_e** and suggests the changes in the polarization of the bond of $2\text{N}(5\text{N})$ $3''\text{C}$ of these tautomers.

Scheme 5



In the ^1H NMR spectrum I_8 after 10 min since preparation of the solution no changes have been observed, after 30 min the resonance line at δ 4.0711, δ 4.0565 are shifted to the lower field δ 4.0735, δ 4.0589, respectively. In the ^1H NMR spectrum I_9 after 20 min the resonance line at

after 20 min

δ 4.0857	δ 4.0882		
δ 4.0711	δ 4.0735		
δ 4.0565	δ 4.0589		
δ 4.0321	δ 4.0345		
δ 4.0174	δ 4.0198		
δ 4.0028	δ 4.0052		

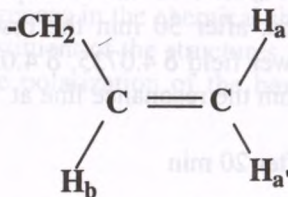
indicate the changes in the structures of **1a_d** **1b_d** **1c_d**, **1a_e** **1b_e** **1c_e** tautomers.

In the ^1H NMR spectrum I a signal of $-\text{N}-\text{CH}_2-$ group appears at δ 3.999 – 4.079 as two triplets as well [1]:

δ 3.999	δ 4.050		
δ 4.013	δ 4.064		
δ 4.027	δ 4.079		

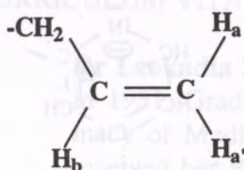
and support the presence of the **1a_d** **1b_d** **1c_d**, **1a_e** **1b_e** **1c_e**, tautomers.

Table 4



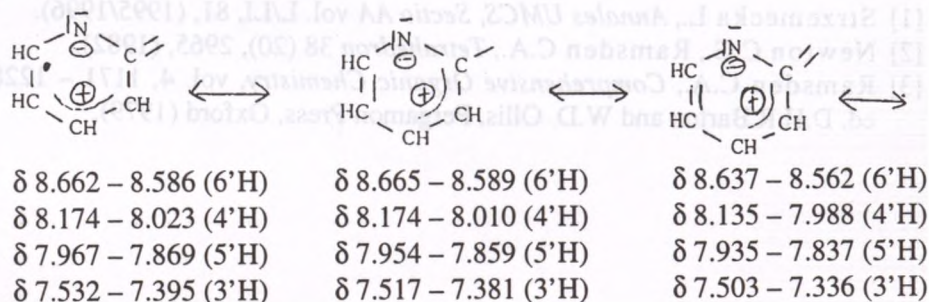
Spec- trum No	H _b							
	1a _d , 1b _d '		1c _d '		1a _e , 1b _e '		1c _e '	
	<i>cis</i> (Z)	<i>trans</i> (E)	<i>cis</i> (Z)	<i>trans</i> (E)	<i>cis</i> (Z)	<i>trans</i> (E)	<i>cis</i> (Z)	<i>trans</i> (E)
I ₆ DMSO	5.997	5.924	6.097	5.824	-	-	-	-
	J(H _b H _d)	J(H _b H _c)	J(H _b H _d)	J(H _b H _c)	-	-	-	-
	7.6Hz	7.6Hz	11.2Hz	18.8Hz	-	-	-	-
	J(H _b H _a ')	J(H _b H _a)	J(H _b H _a ')	J(H _b H _a)	-	-	-	-
8.5Hz	15.4Hz	10.6Hz	17.6Hz	-	-	-	-	
8.2Hz	8.2Hz	8.2Hz	8.2Hz	-	-	-	-	
I ₇ DMSO	6.033	5.96	6.133	5.86	6.033	5.96	6.133	5.86
	J(H _b H _d)	J(H _b H _c)	J(H _b H _d)	J(H _b H _c)	J(H _b H _d)	J(H _b H _c)	J(H _b H _d)	J(H _b H _c)
	7.6Hz	7.6Hz	11.2Hz	18.8Hz	7.8Hz	8.2Hz	7.8Hz	8.2Hz
	J(H _b H _a ')	J(H _b H _a)	J(H _b H _a ')	J(H _b H _a)	-	-	-	-
8.5Hz	15.4Hz	10.6Hz	17.6Hz	-	-	-	-	
I ₁₀ DMSO +D ₂ O	6.029	5.955	6.129	5.855	6.029	5.955	6.129	5.855
	J(H _b H _d)	J(H _b H _c)	J(H _b H _d)	J(H _b H _c)	J(H _b H _d)	J(H _b H _c)	J(H _b H _d)	J(H _b H _c)
	7.6Hz	7.6Hz	11.2Hz	18.8Hz	7.8Hz	8.2Hz	7.8Hz	8.2Hz
	J(H _b H _a ')	J(H _b H _a)	J(H _b H _a ')	J(H _b H _a)	-	-	-	-
8.5Hz	15.4Hz	10.6Hz	17.6Hz	-	-	-	-	
I ₈ CDCl ₃	-	-	-	-	6.007	5.936	6.107	5.836
	-	-	-	-	J(H _b H _d)	J(H _b H _c)	J(H _b H _d)	J(H _b H _c)
	-	-	-	-	7.4Hz	7.5Hz	11.5Hz	18.9Hz
	-	-	-	-	J(H _b H _a ')	J(H _b H _a)	J(H _b H _a ')	J(H _b H _a)
-	-	-	-	8.5Hz	12.3Hz	10.9Hz	17.3Hz	
-	-	-	-	J(H _b H _d)	J(H _b H _c)	J(H _b H _d)	J(H _b H _c)	
-	-	-	-	7.8Hz	8.2Hz	7.8Hz	8.2Hz	
I ₉ CDCl ₃	-	-	-	-	6.007	5.936	6.107	5.836
	-	-	-	-	J(H _b H _d)	J(H _b H _c)	J(H _b H _d)	J(H _b H _c)
	-	-	-	-	7.4Hz	7.5Hz	11.5Hz	18.9Hz
	-	-	-	-	J(H _b H _a ')	J(H _b H _a)	J(H _b H _a ')	J(H _b H _a)
-	-	-	-	8.5Hz	12.3Hz	10.9Hz	17.3Hz	
-	-	-	-	J(H _b H _d)	J(H _b H _c)	J(H _b H _d)	J(H _b H _c)	
-	-	-	-	7.8Hz	8.2Hz	7.8Hz	8.2Hz	

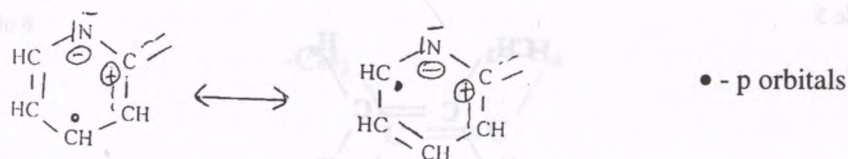
Table 5



Spectrum No solvent	H _a (Z)	tautomer	H _a (E)	tautomer
I ₆ DMSO	5.104 – 5.152 m	1a _d ' 1b _d ' 1c _d ' 1a _d 1b _d 1c _d 1a _e ' 1b _e ' 1c _e ' 1a _e 1b _e 1c _e	5.177 – 5.252 m	1a _d ' 1b _d ' 1c _d ' 1a _d 1b _d 1c _d
			5.348 – 5.399 m	1a _e ' 1b _e ' 1c _e ' 1a _e 1b _e 1c _e
I ₇ DMSO	5.133 – 5.179 m	1a _d ' 1b _d ' 1c _d ' 1a _d 1b _d 1c _d 1a _e ' 1b _e ' 1c _e ' 1a _e 1b _e 1c _e	5.213 – 5.279 m	1a _d ' 1b _d ' 1c _d ' 1a _d 1b _d 1c _d
			5.384 – 5.435 m	1a _e ' 1b _e ' 1c _e ' 1a _e 1b _e 1c _e
I ₁₀ DMSO + D ₂ O	5.143 – 5.189 m	1a _d ' 1b _d ' 1c _d ' 1a _d 1b _d 1c _d 1a _e ' 1b _e ' 1c _e ' 1a _e 1b _e 1c _e	5.208 – 5.289 m	1a _d ' 1b _d ' 1c _d ' 1a _d 1b _d 1c _d
			5.382 – 5.431 m	1a _e ' 1b _e ' 1c _e ' 1a _e 1b _e 1c _e
I ₈ CDCl ₃	5.191 – 5.235 m	1a _d ' 1b _d ' 1c _d ' 1a _d 1b _d 1c _d 1a _e ' 1b _e ' 1c _e ' 1a _e 1b _e 1c _e	5.265 – 5.333 m	1a _d ' 1b _d ' 1c _d ' 1a _d 1b _d 1c _d
			5.435 – 5.482 m	1a _e ' 1b _e ' 1c _e ' 1a _e 1b _e 1c _e
I ₉ CDCl ₃	5.184 – 5.226 m	1a _d ' 1b _d ' 1c _d ' 1a _d 1b _d 1c _d 1a _e ' 1b _e ' 1c _e ' 1a _e 1b _e 1c _e	5.267 – 5.326 m	1a _d ' 1b _d ' 1c _d ' 1a _d 1b _d 1c _d
			5.438 – 5.482 m	1a _e ' 1b _e ' 1c _e ' 1a _e 1b _e 1c _e

Scheme 6





δ 8.606 – 8.530 (6'H)	δ 8.601 – 8.525 (6'H)
δ 8.245 – 8.145 (4'H)	δ 8.237 – 8.137 (4'H)
δ 7.859 – 7.688 (5'H)	δ 7.854 – 7.681 (5'H)
δ 7.349 – 7.212 (3'H)	δ 7.342 – 7.205 (3'H)

The differences in the polarization of the bond of 2N(5N) 3''C may be connected with the differences in the interactions of orbitals of these atoms and may be caused by the differences in the spins states of electrons as well as in the phases of their orbitals. In the structures **1a_e**, **1b_e**, **1c_e**, **1a_e**, **1b_e**, **1c_e** the polarization of this bond may be influenced by 2p orbitals both of 2C(5C) of 1,3,4-thiadiazole ring and of 2''C 1''C of allyl substituent. Consequently, the chemical shifts values of the protons of -N-CH₂- group of allyl substituent depend on the electron configuration of exocyclic nitrogen atom 2N(5N).

In the ¹H NMR spectra I₆₋₁₀ the signals of the protons of the pyridyl substituent (Table 3) indicate the existence of the following mesomeric structures of the pyridine ring (Scheme 6).

3. EXPERIMENTAL

The ¹H NMR spectra I₆₋₁₀ of product **1abc** were measured with a Tesla BS 677 A spectrometer (100 MHz with T. F.) in CDCl₃ or DMSO solutions at room temperature with TMS as the internal standard. Chemical shifts are given in δ scale. Compounds **1abc** were obtained by method I [1].

4. REFERENCES

- [1] Strzemecka L., *Annales UMCS, Sectio AA* vol. L/LI, 81, (1995/1996).
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CURRICULUM VITAE



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