Scientific paper

Tautomerism of Allyl-5-(pyridin-2-yl)-[1,3,4] Thiadiazol-2-yl) Amine

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Abstract

The radical and ionic structures of allyl-(5-pyridin-2-yl-[1,3,4] thiadiazol-2-yl)-amine **1A ↔ 1A' ↔ 1A'$_a$, 1A (I) ↔ 1A (I)' ↔ 1A (I)'$_a$** have been determined by means of its ^{1}H (100 MHz, 500 MHz) ^{13}C and ^{15}N NMR spectra and B3LYP/6-31G** computations. The tautomeric intercorvertions of **1A ↔ 1A (I) ⇒ 1B, 1A ↔ 1A (I) ⇒ 1C** have been observed in the ^{1}H NMR spectra (100 MHz)

Keywords: Allyl-(5-pyridin-2-yl-[1,3,4]-thiadiazol-2-yl)-amine; tautomerism

1. Introduction

The ^{1}H ^{13}C ^{15}N NMR studies of allyl- (**1**) and (3-phenyl-allyl)- (**2**) (5-(pyridin-2-yl)-[1,3,4] thiadiazol-2-yl)-amine and theoretical calculations support ionic and radical structures (Figs 1–4).[1] The XRD data support only one tautomer **a –** type in the crystals of both compounds **1, 2**. In the solid state the *exo*-amino form **a** is stabilized by different H bonds, and the differences in the total energy between tautomers **a** and **b** are equal to –35.6 and –34.3 kJ/mol for **1** and **2**, respectively, according to DFT level of theory calculations.[1] The ^{1}H– data (100 MHz, 500 MHz), ^{13}C–and ^{15}N NMR spectra as well as the theoretical calculations of allyl-(**1**) and (3-phenyl-allyl)-(**2**) (5-pyridin-2-yl-[1,3,4] thiadiazol-2-yl)-amine (tautomer **a** – type) point to the changes of the amine – type **a** nitrogen atom N-6 to pyridine – type **A** and pyrrole – type **A (I)** of **1, 2** and to sp hybridization **A (II)** of **2**. In the range of the chemical shifts of the NH proton from δ 8.665 to 7.233, the ^{1}H NMR (100 MHz) spectra of **1**, **2** there are no

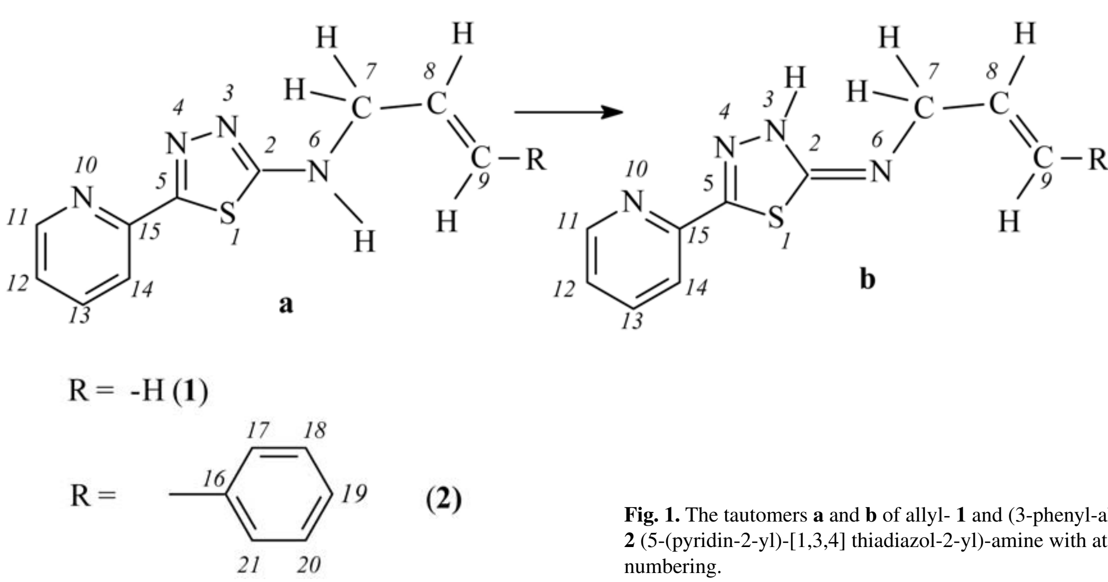


Fig. 1. The tautomers **a** and **b** of allyl- **1** and (3-phenyl-allyl)- **2** (5-(pyridin-2-yl)-[1,3,4] thiadiazol-2-yl)-amine with atom numbering.

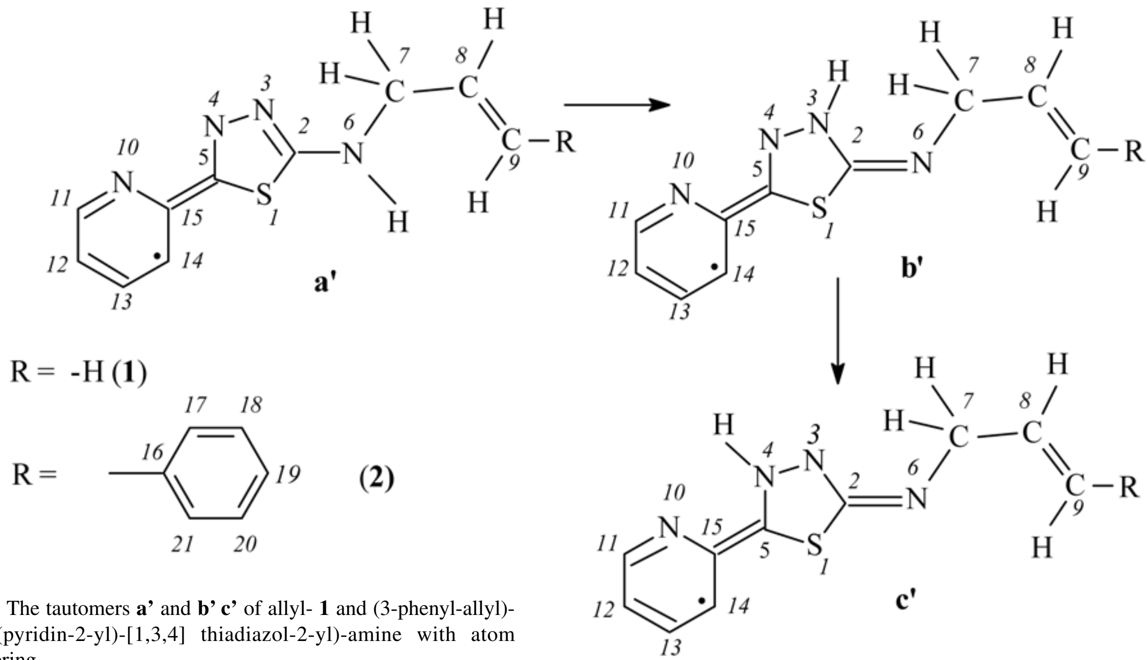


Fig. 2. The tautomers **a'** and **b' c'** of allyl- **1** and (3-phenyl-allyl)-**2** (5-(pyridin-2-yl)-[1,3,4] thiadiazol-2-yl)-amine with atom numbering.

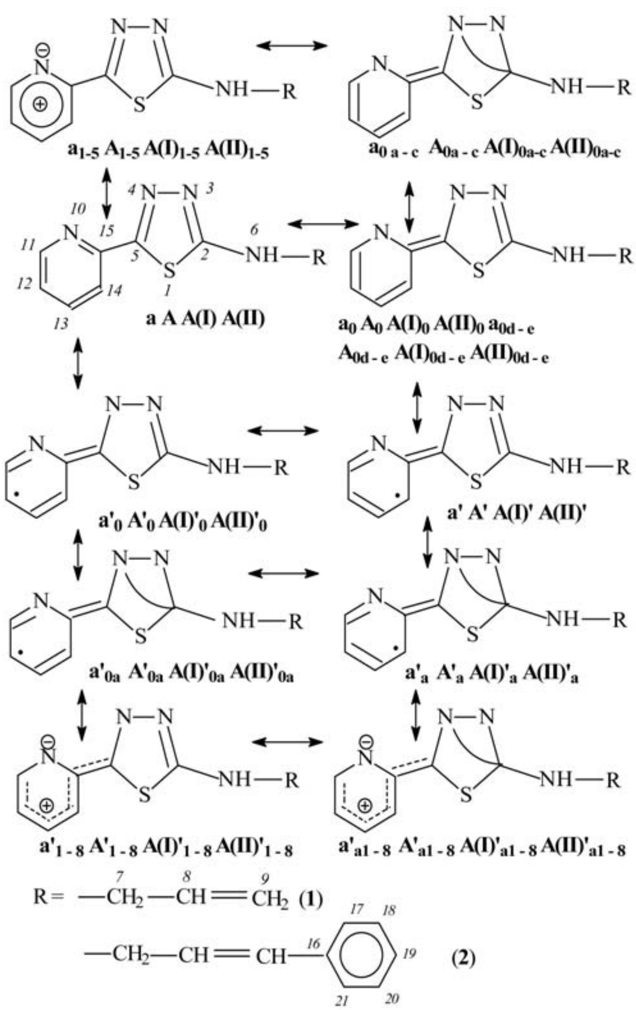


Fig. 3. The resonance structures of allyl-**1** and (3-phenyl-allyl)-**2** (5-pyridin-2-yl)-[1,3,4]thiadiazol-2-yl)-amine.

transitions of electrons of p orbitals of 1S 2C 3N 4N 5C of 1,3,4-thiadiazole ring. The nitrogen atoms N3, N4, N10 appear as pyridine – type, pyrrole – type and amine – type. Due to the changes of the electronic structure of these atoms the radical structures are possible (Fig. 3). The changes of the electronic structure of the nitrogen atoms N3, N4, N10 have been described previously.[2]

Previous 100 MHz ^{1}H NMR investigations of **1, 2** in the solution in the range from δ 8.665 to 7.233 of the chemical shift of N–H proton support the tautomeric equilibrium between allyl – **(1)** (3-phenyl-allyl-) **(2)** (5-pyridin-2-yl-[1,3,4] thiadiazol-2-yl-) amine **1A 1A', 2A (I) 2A (I)', 2A (II) 2A (II)',** 3H allyl- **(1)** (3-phenyl-allyl-) **(2)** (5-pyridin-2-yl-[1,3,4] thiadiazol-2-ylidene-) amine **1B 1B', 2B 2B' 2B (II)'** and 4H allyl- **(1)** (3-phenyl-allyl-) **(2)** (5-pyridin-2-yl-[1,3,4] thiadiazol-2-ylidene-) amine **1C', 2C' 2C (II)'**.[2, 3]

In the ^{1}H NMR spectra 100 MHz of **1, 2** the signals of NH proton in the range of the chemical shifts from δ 8.665 to 7.233 point to the co – existence of two tautomeric forms **1A' ⇒ 1B', 1A' ⇒ 1C', 2A(I)' ⇒ 2B', 2A(II)' ⇒ 2C(II)'**. In the ^{1}H NMR spectra 100 MHz of **1** the intensities of the signals of N-H proton confirm the interconvertions of the $\mathbf{1A'_5 \Rightarrow 1B_3 \Rightarrow 1C'_4}$ as well as the balance of $\mathbf{1A'_7 \Rightarrow 1B'_7}$ and $\mathbf{1A'_7 \Rightarrow 1C'_7}$ tautomers and support pyridine – type nitrogen atoms N-10 N-4 N-6 and the amine – type nitrogen atoms N-4 N-3 of 1,3,4 – thiadiazole ring,[2] respectively. In the ^{1}H NMR spectra of **2** (100 MHz) the interconvertions of $\mathbf{2A(I)'_{1-4} \Rightarrow 2B'_{1-4}\ 2A(II)'_{1-4} \Rightarrow 2C(II)'_{1-4}, 2A(I)'_{6,7} \Rightarrow 2B'_{6,7}, 2A(II)'_{6,7} \Rightarrow 2C(II)'_{6,7}}$ tautomers have been observed and support the amine – type nitrogen atoms N4, N3 of 1,3,4 – thiadiazole ring.[3]

The aim of the present paper was to describe the electronic structure of the nitrogen atoms of **1a** tautomer

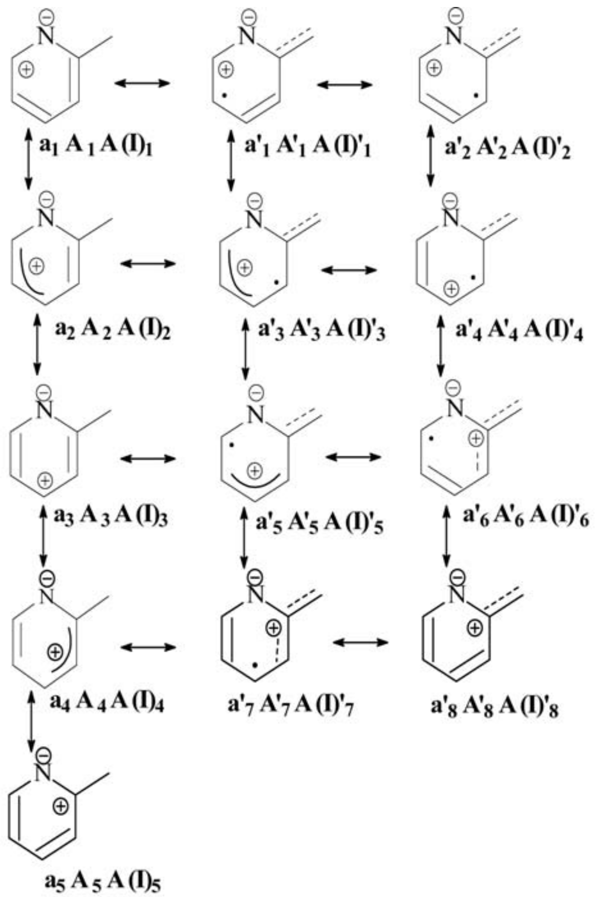


Fig. 4. The resonance structures of the pyridyl substituent.

in the range from δ 7.125–6.500 of the chemical shifts of the N-H proton and its interconvertions to the imino forms in the solution.

The structural studies of the 2-amino-[1,3,4]thiadiazole derivatives have been performed in order to know the properties of the compounds with the determined biological activity. The N6 and/or 5-substituted-2-amino 1, 3, 4-thiadiazoles depending on the nature of substituents show varied pharmacological activity. They have revealed potent activity against the leukemia, melanoma, lung carcinoma. They are also known to be the carbonic anhydrase inhibitors, and some of them possess the antimycobacterial, anesthetic, antidepressant and anxiolytic activity.[4–14] The 2-amino-[1,3,4]thiadiazoles are found in a new class of herbicides with a broad spectrum of activity[15] as well as the corrosion inhibitors.[16]

2. Experimental

The product **1** was prepared according to the published method[17] and its NMR spectra (^{1}H, ^{13}C, ^{15}N) were recorded under various conditions: on Tesla BS 677 A and Bruker AM 500 spectrometers.

The ^{1}H-, ^{13}C- and ^{15}N-NMR measurements of **1** were taken in $CDCl_3$ and in DMSO – d_6 solutions, respectively on a Bruker AM 500 spectrometer, operating at 500.18 MHz for hydrogen, 125.76 MHz for carbon and 50.68 MHz for nitrogen, using standard conditions. The 2D spectra of ^{1}H–^{13}C HMQC, ^{1}H–^{13}C HMBC, ^{1}H–^{1}H COSY (500 MHz) have been recorded in a $CDCl_3$ solution according to procedure given in the Bruker programme library. The ^{1}H-NMR spectra (1–6) of **1** were measured on a Tesla BS 677 A spectrometer (100 MHz with T. F.) in $CDCl_3$ or DMSO solutions at room temperature with TMS as the internal standard. The ^{1}H-NMR spectra 1, 1_3 1_4, 2–6, 6_5, 6_6 (100 MHz) and 1_7 (500 MHz) have been recorded in $CDCl_3$ solution and the spectra 1_1 1_2 (100 MHz) in DMSO solution.[17, 18, 1] The ^{1}H–NMR spectra $1_{1–4}$ (100 MHz)[18] have been taken using various concentration of **1** in DMSO or $CDCl_3$ solutions:

– in a DMSO solution, the concentration of **1** amounts to 1:3 (spectra 1_1 1_2, respectively);
– in a $CDCl_3$ solution, the concentration of **1** amounts to: 10 mg/0.5 ml and 25 mg/0.5 ml (maximal concentration, spectra 1_3 1_4, respectively).

The ^{1}H-NMR spectra 1–6, 6_5 6_6,[17] 1_7[1] and 1_8[18] have been recorded in $CDCl_3$ and DMSO – D_2O solutions, respectively, without any determination of the concentration of **1**. In the ^{1}H-NMR spectra 1–6 of **1** the signals of the protons of allyl, pyridyl substituents as well as of NH proton of 1,3,4-thiadiazole have been recorded. In the ^{1}H-NMR spectra 6_5 6_6 of **1**[17] only the signals of the NH proton of the 1,3,4-thiadiazole have been recorded.

The molecular geometries and properties corresponding to the local minima of the energy were calculated[1] at the DFT level of the theory with the B3LYP density functional and the 6-31G** basis set.[19, 20] The same basis set and functional were used for the ^{1}H-, ^{13}C- and ^{15}N-NMR shielding constants calculations by applying the GIAO CPHF methods. The atomic charges were taken from the ESP fit using Breneman model (CHELPG). The Gaussian 98 package[21] was employed for these calculations.

3. Results and Discussion

The calculated chemical shifts of the nitrogen atoms ^{15}N for **a** – type and **b** – type tautomers occur in the different ranges: from about δ – 309 to about – 23 for **a** – type tautomer and from about δ – 225 to about – 80 for **b**-one (Table 1, Fig. 5).[1] The shielding constants for the N3 and N10 atom in the 1,3,4 – thiadiazole and pyridine rings, respectively are almost equal whereas N4 atom is much less shielded.[1] The amino N6 atom is strongly shielded in **1** (about δ – 308) but in **2** the shielding decreases by a few ppm (to about δ – 304). The value of the chemical shift for the NH proton of **1** recorded in $CDCl_3$ solution at 500,16 MHz, δ 5.81 ppm[1] is in agreement with the resonanses of the amino protons. In ^{15}N NMR spectrum of **1** the signal of the nitrogen

Table 1. Calculated ^{15}N and ^{1}H NMR chemical shifts δ [ppm] of type **a** and **b** tautomers

Comp.	^{15}**N**	^{1}**H**	
1a 2a	– 309 – –23		
1a	N6 – 131.57	H 14	8.125
	N3 – 77.78		
2a	N10 – 86.0	H 6	7.5
	N6 – 133.98		
1b 2b	– 225 – –80		

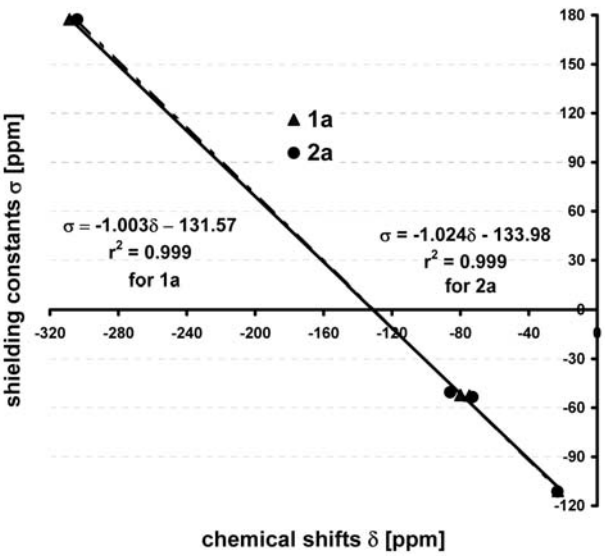


Fig. 5. The linear regression of shielding constants ó [ppm] versus chemical shifts δ [ppm] for **1a** and **2a**.

atom N6 at δ – 308.58[1] supports the amino – type nitrogen. The calculated chemical shift of the nitrogen atom N6 δ – 131.57 confirms pyridine – type nitrogen atom (Table 1).

In the ^{15}N-NMR spectrum of **1** the chemical shift of N10 at δ – 80.01[1] supports pyrrole – type nitrogen atom of the pyridyl substituent. The calculated chemical shift value of N3 at δ – 77.78 and ^{13}C resonances line of C2 at δ 171.42 in ^{13}C NMR spectrum [1] confirm pyridine – type nitrogen atom of **1**. The ^{1}H –^{13}C HMQC correlation spectra show a correlation signal between H14 at δ 8.360 and C15 at δ 149.7[2]. The above data prove the existence of the diradical resonance structures $\mathbf{a_0}$ $\mathbf{A_0}$ $\mathbf{A\ (I)_0}$ $\mathbf{A\ (II)_0}$ $\mathbf{a'_0}$ $\mathbf{A'_0}$ $\mathbf{A\ (I)'_0}$ $\mathbf{A\ (II)'_0}$, (Figs 3, 6).

The calculated signal at δ 8,125 (H14) of **1** (Table 1) as well as the coupling constants $J(H_{12}H_{14})$ 1,0 Hz $J(H_{11}H_{14})$ 0,5 Hz[1] confirm the lack of the charges on the pyridine ring. In the 2D ^{1}H ^{13}C HMBC spectra of **1** the cross – peaks between H14 and C14 at δ 8.150, δ 119.9 support the structures **a A A (I) A (II)** (Figs 3, 6).

The calculated chemical shift of N10 at δ – 86.0 of **2** (Table 1)[1] points to an amine – type nitrogen atom. The ^{1}H

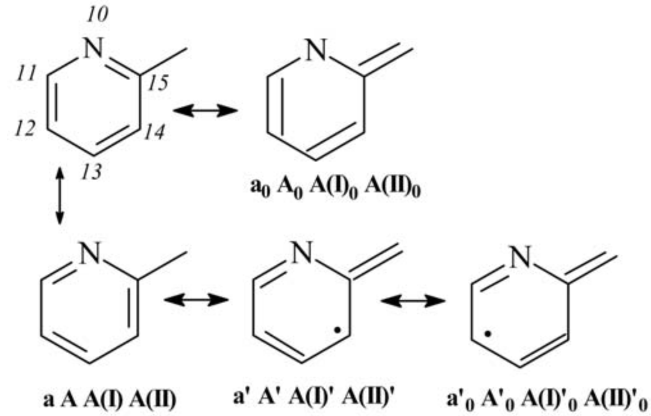


Fig. 6. The resonance structures of the pyridyl substituent

^{13}C HMQC correlation spectra of **2** show a correlation signal between H-14 at δ 8.290 and C15 at δ 149.7. The above data prove the diradical resonance structures $\mathbf{a_{0c}}$ $\mathbf{A_{0c}}$ $\mathbf{A(I)_{0c}}$ $\mathbf{A(II)_{0c}}$, $\mathbf{a_{0e}}$ $\mathbf{A_{0e}}$ $\mathbf{A(I)_{0e}}$ $\mathbf{A(II)_{0e}}$ (Fig. 3) and the lack of the charges over pyridine and 1,3,4-thiadiazole rings.[3]

The pyridyl H14 proton of the diradical resonance structures $\mathbf{a_0}$ $\mathbf{A_0}$ $\mathbf{A(I)_0}$ $\mathbf{A(II)_0}$ $\mathbf{a'_0}$ $\mathbf{A'_0}$ $\mathbf{A(I)'_0}$ $\mathbf{A(II)'_0}$ and $\mathbf{a_{0c}}$ $\mathbf{A_{0c}}$ $\mathbf{A(I)_{0c}}$ $\mathbf{A(II)_{0c}}$, $\mathbf{a_{0e}}$ $\mathbf{A_{0e}}$ $\mathbf{A(I)_{0e}}$ $\mathbf{A(II)_{0e}}$ is more intensely deshielded by about 0.2 ppm and 0.15 ppm in relation to the structures **a A A(I) A(II)**, respectively. The spectroscopic data support the conjugation of the aromatic π electrons of the pyridyl substituent with the π electrons of the C = N double bond of the 1,3,4 thiadiazole ring in the solution.

The signals of the NH proton and the pyridyl substituent in the ^{1}H NMR spectra (100 MHz) of **1** support the ionic **a A A(I)**, $\mathbf{a_{1–5}}$, $\mathbf{A_{1–5}}$ $\mathbf{A(I)_{1–5}}$ and radical resonance structures $\mathbf{a'_{1–8}}$, $\mathbf{A'_{1–8}}$ $\mathbf{A(I)'_{1–8}}$, **a' A' A(I)'** $\mathbf{a'_0}$ $\mathbf{A'_0}$ $\mathbf{A(I)'_0}$ (Figs 1–4, 6, Tables 2–11). The resonance structures of the pyridine ring are shown on Fig. 4.

In the ^{13}C-NMR spectrum of **1** the chemical shifts of C11 at δ 149.31 and C15 at δ 149.87[1] confirm pyridine – type nitrogen atom N10 of the structures $\mathbf{a_1}$ $\mathbf{A_1}$ $\mathbf{A(I)_1}$ $\mathbf{a'_1}$ $\mathbf{A'_1}$ $\mathbf{A(I)'_1}$ $\mathbf{a'_2}$ $\mathbf{A'_2}$ $\mathbf{A(I)'_2}$ and $\mathbf{a_5}$ $\mathbf{A_5}$ $\mathbf{A(I)_5}$, respectively. The chemical shift of C12 at δ 124.01 [1] supports the pyridine – type nitrogen atom N10 of the structures $\mathbf{a_2}$ $\mathbf{A_2}$ $\mathbf{A(I)_2}$ $\mathbf{a'_3}$ $\mathbf{A'_3}$ $\mathbf{A(I)'_3}$ $\mathbf{a'_5}$ $\mathbf{A'_5}$ $\mathbf{A(I)'_5}$. The signal of C14 at δ 119.87[1] points to the structures $\mathbf{a_3}$ $\mathbf{A_3}$ $\mathbf{A(I)_3}$ $\mathbf{a'_4}$ $\mathbf{A'_4}$ $\mathbf{A(I)'_4}$ $\mathbf{a_5}$ $\mathbf{A_5}$ $\mathbf{A(I)_5}$. The signal of C13 at δ 136.77[1] confirms the structures $\mathbf{a_2}$ $\mathbf{A_2}$ $\mathbf{A(I)_2}$ $\mathbf{a'_3}$ $\mathbf{A'_3}$ $\mathbf{A(I)'_3}$ $\mathbf{a_4}$ $\mathbf{A_4}$ $\mathbf{A(I)_4}$ $\mathbf{a'_5}$ $\mathbf{A'_5}$ $\mathbf{A(I)'_5}$.

The ^{1}H-NMR spectrum 1_7 (500 MHz) shows the signal of H14 of the structures $\mathbf{a'_1}$ $\mathbf{A'_1}$ $\mathbf{A\ (I)'_1}$ $\mathbf{a'_5}$ $\mathbf{A'_5}$ $\mathbf{A(I)'_5}$ $\mathbf{a'_6}$ $\mathbf{A'_6}$ $\mathbf{A(I)'_6}$ at δ 8.185. In the ^{1}H-^{13}C HMBC and HMQC correlatinon spectra the signal of H14 at δ 8.180 exhibits a correlation to C14 at δ 119.7 and C12 at δ 124.0, C15 at δ 149.7, C5 at δ 160.0, respectively and confirms $\mathbf{a'_5}$ $\mathbf{A'_5}$ $\mathbf{A(I)'_5}$ $\mathbf{a'_6}$ $\mathbf{A'_6}$ $\mathbf{A(I)'_6}$ structures. In the 2D ^{1}H-^{13}C HMQC spectra the cross – peak between H11 at δ 8.340 and C14

Table 2. The [1]H NMR chemical shifts δ [ppm] from TMS of **1**.

Spectrum No / Solvent	H 7	H 8	H 9	Pyridin–2–yl
1_1 DMSO	3.922 – 4.061 2H m	5.772 – 6.148 1H m	5.104 – 5.399 2H m	8.637 – 8.562 1H H 11 8.135 – 7.988 1H H 13 H 14 7.935 – 7.837 1H H 12 H 13 7.503 – 7.336 1H H 14 H 12
1_2 DMSO	3.988 – 4.086 2H m	5.809 – 6.187 1H m	5.133 – 5.435 2H m	8.665 – 8.589 1H H 11 8.174 – 8.010 1H H 13 H 14 7.954 – 7.859 1H H 12 H 13 7.517 – 7.381 1H H 14 H 12
1_3 $CDCl_3$	4.003 – 4.086 2H m	5.782 – 6.160 1H m	5.191 – 5.482 2H m	8.606 – 8.530 1H H 11 8.245 – 8.145 1H H 13 H 14 7.859 – 7.688 1H H 12 H 13 7.349 – 7.212 1H H 14 H 12
1_4 $CDCl_3$	4.003 – 4.086 2H m	5.782 – 6.160 1H m	5.191 – 5.482 2H m	8.601 – 8.525 1H H 11 8.237 – 8.137 1H H 13 H 14 7.854 – 7.681 1H H 12 H 13 7.342 – 7.205 1H H 14 H 12
1_8 DMSO – D_2O	4.069 – 3.988 2.5H m	5.804 – 6.180 1.14H m	5.143 – 5.431 2.21H m	8.662 – 8.586 1.07H H 11 8.174 – 8.023 1H H 13 H 14 7.967 – 7.869 1.42H H 12 H 13 7.532 – 7.395 1.21H H 14 H 12

Table 3. The [1]H NMR chemical shifts δ [ppm] from TMS of **1**

Spectrum No Solvent	H 7	H 8	H 9	Pyridin – 2– yl
1 $CDCl_3$	4.079 – 3.999 2H	6.101 – 5.778 1H	5.458 – 5.196 2H	8.594 – 8.519 1H H 11 8.232 – 8.143 1H H 13 H 14 7.847 – 7.674 1H H 12 H 13 7.336 – 7.200 1H H 14 H 12
2 $CDCl_3$	4.083 – 4.003 2H	6.106 – 5.782 1H	5.463 – 5.196 2H	8.580 – 8.537 1H H 11 8.237 – 8.148 1H H 13 H 14 7.847 – 7.674 1H H 12 H 13 7.336 – 7.200 1H H 14 H 12
3 $CDCl_3$	4.088 – 4.003 2H	6.111 – 5.787 1H	5.477 – 5.182 2H	8.598 – 8.537 1H H 11 8.237 – 8.148 1H H 13 H 14 7.847 – 7.674 1H H 12 H 13 7.331 – 7.195 1H H 14 H 12
4 $CDCl_3$	4.088 – 4.003 2H	6.111 – 5.787 1H	5.482 – 5.186 2H	8.603 – 8.528 1H H 11 8.242 – 8.152 1H H 13 H 14 7.852 – 7.683 1H H 12 H 13 7.341 – 7.204 1H H 14 H 12
5 $CDCl_3$	4.088 – 4.008 2H	6.101 – 5.778 1H	5.468 – 5.177 2H	8.589 – 8.514 1H H 11 8.387 – 8.345 1H H 11 8.223 – 8.143 1H H 13 H 14 8.077 – 7.974 1H H 13 H 14 7.838 – 7.646 2H H 12 H 13 7.397 – 7.143 2H H 14 H 12
6 $CDCl_3$	4.083 – 4.003 2H	6.106 – 5.782 1H	5.482 – 5.196 2H	8.598 – 8.523 1H H 11 8.228 – 8.138 1H H 13 H 14 7.852 – 7.678 1H H 12 H 13 7.336 – 7.200 1H H 14 H 12

at δ 119.9 as well as the correlation signals of H11 at δ 8.360 to C14 at δ 119.9 , C15 at δ 149,7 support structures **a'$_2$ A'$_2$ A(I)'$_2$ a$_1$ A$_1$ A(I)$_1$.** The chemical shift of N10 in ^{15}N-NMR spectrum of **1** at δ – 74.78 supports the structures **a$_2$ A$_2$ A(I)$_2$, a'$_3$ A'$_3$ A(I)'$_3$, a$_4$ A$_4$ A(I)$_4$, a'$_{5–8}$ A'$_{5–8}$ A(I)'$_{5–8}$**.

The ^{1}H–^{1}H coupling constants J(H$_{14}$H$_{13}$) 8.0 Hz J(H$_{13}$H$_{14}$) 8.0 Hz J(H$_{12}$H$_{13}$) 8.0 Hz[1] of **1a** tautomer confirm the positive charge at C13 atom of the structures **a$_3$ A$_3$ A(I)$_3$ a'$_4$ A'$_4$ A(I)'$_4$** while the coupling constants J(H$_{12}$H$_{13}$) 5.8 Hz J(H$_{11}$H$_{12}$) 5.6 Hz J(H$_{13}$H$_{11}$) 1.6 Hz[1] indicate the positive charge at C15 and the negative one at N10 atoms of pyridine substituent of the structures **a$_4$ A$_4$ A(I)$_4$ a'$_7$ A'$_7$ A(I)'$_7$**.

In the range of the chemical shifts of NH proton from δ 7.125 to – 0.033 the transitions of electrons of 2p orbitals of C2 N3 N4 C5 and of 3p of S1 occur. In the ^{1}H NMR spectra of **1** the chemical shifts of NH proton in the range from δ 7.125 to 6.500 ppm point to the transitions of electrons of p orbitals of the following polar structures:

- **1A'(1) ↔ 1A (I)'(1) 1A'$_0$ (1) ↔ 1A (I)'$_0$ (1) 1A$_0$ (1) ↔ 1A (I)$_0$ (1), 1A (2) ↔ 1A (I)(2) 1A'(2) ↔ 1A (I)'(2) 1A'$_0$ (2) ↔ 1A (I)'$_0$ (2) 1A$_0$ (2) ↔ 1A (I)$_0$ (2), 1A (3) ↔ 1A (I)(3), 1A (4) ↔ 1A (I)(4)** (Fig. 7),
- **1A (5) ↔ 1A (I) (5), 1A'(5) ↔ 1A (I)'(5), 1A'$_0$ (5) ↔ 1A (I)'$_0$ (5), 1A$_0$ (5) ↔ 1A (I)$_0$ (5), 1A (6) ↔ 1A (I) (6), 1A'(6) ↔ 1A (I)'(6), 1A'$_0$ (6) ↔ 1A(I)'$_0$ (6), 1A$_0$ (6) ↔ 1A (I)$_0$ (6)** (Fig. 8),
- **1B (2) 1B'(2) 1B'$_0$ (2) 1B$_0$ (2), 1B'(1) 1B'$_0$ (1) 1B$_0$ (1), 1B (3), 1B (4)** (Fig. 9), **1B (5) 1B'(5) 1B'$_0$ (5) 1B$_0$ (5), 1B (5) 1B (2) 1B'(1)** (Fig. 10), **1C (6) 1C (5) 1C (4)** (Fig. 10),
- **1C (2) 1C'(2) 1C'$_0$ (2) 1C$_0$ (2), 1C (4), 1C (3), 1C'(5) 1C'$_0$ (5) 1C$_0$ (5) 1C (5)** (Fig. 11).

In the ^{1}H NMR spectra (100 MHz) of **1a** tautomer in the range from δ 7.125 to 6.500 the nitrogen atoms N3, N4, N10 appear as pyridine – type, pyrrole – type nitrogen while N6 as pyridine – type **A**, pyrrole – type **A(I)** or in sp hybridization **A(II)**.

In the ^{1}H NMR spectrum 1$_1$ of **1** (100 MHz, DMSO) the signal of H7 arises as three doublets of doublets at δ 3.922–3.954, δ 3.978–4.008, δ 4.032–4.061 (Figs 12, 13).

At the chemical shift δ 3.922–3.954 (dd) the electrons of 2p orbitals of N6 C7 show differences in their spin states. The differences in the coupling constants J(H$_8$H$_{9B}$) 17.6 Hz J(H$_8$H$_{7C}$) 18.8Hz, J(H$_8$H$_{9A}$) 10.6Hz J(H$_8$H$_{7D}$) 11.2Hz (100 MHz)[18] and the ^{13}C NMR signals of allyl substituent C9 at δ 117.99, C8 at δ 132.80, C7 at δ

Table 4. The ^{1}H NMR chemical shifts δ [ppm] from TMS of **1**.

Spectrum No Solvent	Pyridin – 2– yl		
	H 14 – of the structures	**H 14, H 13**	**H 13** – of the structures
1$_3$(CDCl$_3$)	**a'$_1$A'$_1$↔ a'$_2$A'$_2$ ↔a'$_0$A'$_0$**	8.245 – 8.145	**a'$_1$A'$_1$ ↔ a'$_2$A'$_2$**
1$_4$(CDCl$_3$)	**a'$_3$A'$_3$ ↔ a'$_1$A'$_1$**	8.237 – 8.137	**a$_2$A$_2$ ↔ a'$_3$A'$_3$**
4(CDCl$_3$)	**a'$_2$A'$_2$ ↔ a'$_1$A'$_1$ ↔ a'$_0$ A'$_0$**	8.242 – 8.152	**a$_1$A$_1$ ↔ a'$_1$A'$_1$ ↔ a A**
2, 3(CDCl$_3$)	**a'$_3$A'$_3$ ↔ a'$_1$A'$_1$ ↔ a'$_0$A'$_0$**	8.237 – 8.148	**a$_2$A$_2$ ↔ a'A'**
1(CDCl$_3$)	**a'$_4$A'$_4$ ↔ a'$_1$A'$_1$ ↔ a'$_0$A'$_0$**	8.232 – 8.143	**a'$_3$A'$_3$ ↔ a'A'**
5(CDCl$_3$)	**a$_4$A$_4$ ↔ a'$_1$A'$_1$ ↔ a'$_0$A'$_0$**	8.223 – 8.143	**a$_4$A$_4$ ↔ a'$_3$A'$_3$ ↔ a'A'**
6(CDCl$_3$)	**a$_2$A$_2$ ↔ a$_4$A$_4$ ↔ a'$_1$A'$_1$**	8.228 – 8.138	**a$_2$A$_2$ ↔ a$_4$A$_4$ ↔ a'$_3$ A'$_3$**
1$_8$(DMSO–D$_2$O)	**a'$_4$A'$_4$ ↔ a'$_5$A'$_5$**	8.174 – 8.023	**a$_4$A$_4$ ↔ a'$_3$A'$_3$**
1$_2$(DMSO)	**a'$_4$A'$_4$ ↔ a'$_6$ A'$_6$**	8.174 – 8.010	**a$_4$A$_4$ ↔ a'$_5$A'$_5$**
1$_1$(DMSO)	**a'$_5$A'$_5$↔ a'$_6$A'$_6$ ↔ a'$_7$A'$_7$**	8.135 – 7.998	**a'$_5$A'$_5$ ↔ a'$_3$A'$_3$**
5(CDCl$_3$)	**a'$_8$A'$_8$ ↔ a'$_6$A'$_6$ ↔ a'$_7$A'$_7$**	8.077 – 7.974	**a'$_3$A'$_3$ ↔ a'$_5$A'$_5$ ↔ a'$_4$A'$_4$**

Table 5. The ^{1}H–NMR chemical shifts δ [ppm] from TMS of **1**.

Spectrum No Solvent	Pyridin – 2– yl		
	H 13 – of the structures	**H 13, H 12**	**H 12** – of the structures
1$_8$(DMSO–D$_2$O)	**a$_3$A$_3$ ↔ a'$_3$A'$_3$ ↔ aA**	7.967 – 7.869	**a$_5$A$_5$ ↔ a$_1$A$_1$ ↔ a'$_8$A'$_8$ ↔ aA**
1$_2$(DMSO)	**a'$_3$A'$_3$ ↔ a'$_5$A'$_5$ ↔ aA**	7.954 – 7.859	**a'$_8$A'$_8$ ↔ a'$_7$A'$_7$**
1$_1$(DMSO)	**a'$_4$A'$_4$ ↔ a'$_5$A'$_5$ ↔ aA**	7.935 – 7.837	**a'$_7$A'$_7$ ↔ a'$_6$A'$_6$**
1$_3$(CDCl$_3$)	**a'$_5$A'$_5$ ↔ a'$_3$A'$_3$ ↔ a'$_0$A'$_0$**	7.859 – 7.688	**a'$_7$A'$_7$ ↔ a'$_1$A'$_1$ ↔ aA**
1$_4$(CDCl$_3$)	**a'$_3$A'$_3$ ↔ a'$_5$A'$_5$**	7.854 – 7.681	**a$_1$A$_1$ ↔ a'$_2$A'$_2$ ↔ a'A'**
4(CDCl$_3$)	**a'$_3$A'$_3$ ↔ a'$_4$A'$_4$ ↔ a'$_0$A'$_0$**	7.852 – 7.683	**a$_2$A$_2$ ↔ a'$_2$A'$_2$ ↔ aA**
6(CDCl$_3$)	**a'$_3$A'$_3$ ↔ a'$_4$A'$_4$**	7.852 – 7.678	**a$_2$A$_2$ ↔ a'$_1$A'$_1$**
1 – 3(CDCl$_3$)	**a'$_3$A'$_3$ ↔ a'$_5$A'$_5$ ↔ a'$_4$A'$_4$**	7.847 – 7.674	**a'$_1$A'$_1$ ↔ a'$_2$A'$_2$**
5(CDCl$_3$)	**a'$_5$A'$_5$ ↔ a'$_4$A'$_4$**	7.838 – 7.646	**a'$_6$A'$_6$ ↔ a'$_1$A'$_1$ ↔ a'$_3$A'$_3$**

Table 6. The [1]H–NMR chemical shifts δ [ppm] from TMS of **1**.

Spectrum No / Solvent	**Pyridin – 2– yl**		
	H 12 – of the structures	**H 12, H 14**	**H 14** – of the structures
1_8(DMSO–D_2O)	$\mathbf{a_5A_5 \leftrightarrow a_4A_4 \leftrightarrow a'_6A'_6 \leftrightarrow a'_0A'_0}$	7.532 – 7.395	$\mathbf{a_1A_1 \leftrightarrow a'_1A'_1 \leftrightarrow aA}$
1_2(DMSO)	$\mathbf{a'_7A'_7 \leftrightarrow a'_1A'_1 \leftrightarrow a'_6A'_6 \leftrightarrow a'_0A'_0}$	7.517 – 7.381	$\mathbf{a_2A_2 \leftrightarrow a'_3A'_3 \leftrightarrow aA}$
1_1(DMSO)	$\mathbf{a'_7A'_7 \leftrightarrow a'_4A'_4 \leftrightarrow a'_0A'_0}$	7.503 – 7.336	$\mathbf{a_2A_2 \leftrightarrow a'_4A'_4 \leftrightarrow aA}$
1_3($CDCl_3$)	$\mathbf{a'_4A'_4 \leftrightarrow a'_2A'_2 \leftrightarrow a_1A_1}$	7.349 – 7.212	$\mathbf{a'_3A'_3 \leftrightarrow a'A'}$
1_4($CDCl_3$)	$\mathbf{a'_4A'_4 \leftrightarrow a'_1A'_1 \leftrightarrow a'_0A'_0}$	7.342 – 7.205	$\mathbf{a'_4A'_4 \leftrightarrow a'A'}$
5($CDCl_3$)	$\mathbf{a'_7A'_7 \leftrightarrow a'_4A'_4 \leftrightarrow a'_2A'_2}$ $\mathbf{\leftrightarrow a'_1A'_1 \leftrightarrow a'_5A'_5 \leftrightarrow a'_3A'_3}$	7.397 – 7.143	$\mathbf{a'_1A'_1 \leftrightarrow a'_3A'_3 \leftrightarrow a'_4A'_4}$ $\mathbf{a'_5A'_5 \leftrightarrow a'_6A'_6 \leftrightarrow a'_7A'_7}$
4($CDCl_3$)	$\mathbf{a'_4A'_4 \leftrightarrow a'_3A'_3 \leftrightarrow a'_1A'_1}$	7.341 – 7.204	$\mathbf{a'_4A'_4 \leftrightarrow aA}$
1, 2, 6($CDCl_3$)	$\mathbf{a'_2A'_2 \leftrightarrow a'_5A'_5 \leftrightarrow a'_0A'_0}$	7.336 – 7.200	$\mathbf{a'_4A'_4 \leftrightarrow a'A' \leftrightarrow a'_5A'_5}$
3($CDCl_3$)	$\mathbf{a'_1A'_1 \leftrightarrow a'_5A'_5}$	7.331 – 7.195	$\mathbf{a'_5A'_5 \leftrightarrow a'A' \leftrightarrow a'_6A'_6}$

Table 7. The 1H–NMR chemical shifts δ [ppm] from TMS of **1**.

Spectrum No Solvent	**Pyridin – 2– yl**	
	H 11	structures
1_2(DMSO)	8.665 – 8.589	$\mathbf{a_4A_4 \leftrightarrow a'_4A'_4 \leftrightarrow a'_7A'_7 \leftrightarrow aA}$
1_8(DMSO–D_2O)	8.662 – 8.586	$\mathbf{a_4A_4 \leftrightarrow a'_6A'_6 \leftrightarrow aA}$
1_1(DMSO)	8.637 – 8.562	$\mathbf{a_3A_3 \leftrightarrow a_5A_5 \leftrightarrow a'_6A'_6}$
1_3($CDCl_3$)	8.606 – 8.530	$\mathbf{a'_7A'_7 \leftrightarrow a'_1A'_1 \leftrightarrow a'_8A'_8 \leftrightarrow aA}$
4($CDCl_3$)	8.603 – 8.528	$\mathbf{a'_4A'_4 \leftrightarrow a'_5A'_5 \leftrightarrow aA}$
1_4($CDCl_3$)	8.601 – 8.525	$\mathbf{a'_6A'_6 \leftrightarrow a'_3A'_3 \leftrightarrow aA}$
3($CDCl_3$)	8.598 – 8.537	$\mathbf{a'_5A'_5 \leftrightarrow a'_8A'_8 \leftrightarrow aA}$
6($CDCl_3$)	8.598 – 8.523	$\mathbf{a'_5A'_5 \leftrightarrow a'A'}$
1($CDCl_3$)	8.594 – 8.519	$\mathbf{a'_5A'_5 \leftrightarrow a'_3A'_3 \leftrightarrow a'_0A'_0}$
5($CDCl_3$)	8.589 – 8.514	$\mathbf{a'_3A'_3 \leftrightarrow a'A'}$
2($CDCl_3$)	8.580 – 8.537	$\mathbf{a'_3A'_3 \leftrightarrow a'_5A'_5 \leftrightarrow a'_8A'_8 \leftrightarrow aA}$
5($CDCl_3$)	8.387 – 8.345	$\mathbf{a'_1A'_1 \leftrightarrow a'_2A'_2 \leftrightarrow a_1A_1}$

Table 8. The [1]H NMR chemical shifts δ [ppm] from TMS of the NH proton of **1A 1A(I), 1A' 1A(I)', 1B 1B', 1C 1C'** tautomers

Spectrum No, ($CDCl_3$)	**δ**	**NH**	**Structure**
6_5	7.125	2.05H	**1A (2, 3) ↔ 1A (I) (2,3) ⇒ 1B (2–4)** **1A (4) ↔ 1A(I)(4) ⇒ 1C (6)**
6_5	7.040	0.786H	**1A (2, 3, 4)$_5$ ↔ 1A (I)(2,3,4)$_5$, 1B (2,3,4)$_5$, 1C (2,3,4)$_5$**
6_6	7.120	3.03H	**1A (5) ↔ 1A (I) (5) ⇒ 1B (5)** **1A (6) ↔ 1A (I)(6) ⇒ 1C (6)**
6_6	7.035	0.802H	**1A (5)$_5$ ↔ 1A (I) (5)$_5$, 1A (6)$_5$ ↔ 1A(I)(6)$_5$, 1B (5)$_5$, 1C (6)$_5$ 1C (5)$_5$**
1_4	6.771	1H s	**1A' (1, 2) ↔ 1A (I)' (1, 2), 1A'(5) ↔ 1A (I)'(5), 1A'(6) ↔ 1A(I)'(6), 1B'(1, 2, 5), 1C'(2, 5)**
1 *	6.750 (H 3) 7.8 (H 12)		**1B'(1, 2, 5)$_2$**
3	6.683	1H s	**1A' (1, 2)$_{2,3}$, ↔ 1A (I)' (1, 2)$_{2,3}$, 1A' (5)$_{2,3}$ ↔ 1A (I)' (5)$_{2,3}$, 1A'(6)$_{2,3}$ ↔ 1A(I)'(6)$_{2,3}$,**
5	6.683	1.142H s	**1B' (1, 2, 5)$_{2,3,}$ 1C' (2, 5)$_{2,3}$**
2	6.674	1H s	**1A' (1, 2)$_{4,5,}$ ↔ 1A (I)'(1, 2)$_{4,5}$, 1A' (5)$_{4,5}$ ↔ 1A (I)' (5)$_{4,5}$, 1A'(6)$_{4,5}$ ↔ 1A(I)'(6)$_{4,5}$, 1B'(1, 2, 5)$_{4,5}$, 1C'(2, 5)$_{4,5}$**
1	6.657	1H s	**1A' (1, 2)$_6$ ↔ 1A (I)' (1, 2)$_6$, 1A' (5)$_6$ ↔ 1A (I)' (5)$_6$, 1A'(6)$_6$ ↔ 1A(I)'(6)$_6$, 1B'(1, 2, 5)$_6$, 1C'(2, 5)$_6$**
6	6.632	1H s	**1A' (1, 2)$_7$ ↔ 1A (I)' (1, 2)$_7$, 1A' (5)$_7$ ↔ 1A (I)' (5)$_7$, 1A'(6)$_7$ ↔ 1A(I)'(6)$_7$, 1B'(1, 2, 5)$_7$, 1C'(2, 5)$_7$**
4	6.500	1.009H s	**1A' (2)$_8$, ↔ 1A (I)' (2)$_8$, 1A' (5)$_8$ ↔ 1A (I)'(5)$_8$, 1A'(6)$_8$ ↔ 1A(I)'(6)$_8$, 1B'(1, 2, 5)$_8$, 1C'(2)$_8$**

* 2D [1]H [1]H COSY spectrum of **1**

49.28[1] support the negatively charged pyridine – type nitrogen atom and positively charged allyl cation. The nitrogen atom N6, the pyridine – type, is occupied with eight electrons. The coupling constants $J(H_8H_{9B})$ 17.6 Hz, $J(H_8H_{9A})$ 10.6Hz $J(H_8H_{9B})$ 17.3 Hz $J(H_8H_{9A})$ 10.9 Hz (100 MHz)[18] $J(H_{9B}H_{9A})$ 1.2 Hz (500 MHz)[1] point to the differences in the spin states of electrons of 2p orbitals of pyridine – type nitrogen and carbon atoms N6 C7 of **1**. At the chemical shifts δ 3.978–4.008 (dd), the electrons of 2p orbitals of N6 C7 show no differences in their spin states. The coupling constants $J(H_8H_{9B})$ 17.1 Hz $J(H_{9B}H_8)$ 17.1 Hz, $J(H_8H_{9A})$ 10.1 Hz $J(H_{9A}H_8)$ 10.1 Hz, $J(H_{9B}H_{9A})$ 1.0 Hz (500 MHz)[1] point to the lack of the differences in the spin states of electrons of 2p orbitals of pyridine – type nitrogen atom N6 C7 of **1**, **s**tructure **A**, the exocyclic nitrogen atom N6 is surrounded by seven electrons.. The magnitude of the couplings $J(H_7H_8) = J(H_8H_7)$ 5.6 Hz (500 MHz)[1] for **1** confirms pyrrole – type nitrogen atom N6, structures **1A (I) 1A (I)$_0$ 1A (I)'$_0$ 1A (I)'** and the possible transformation of $sp^2 \Leftrightarrow$ sp hybridization, the structures **1A (I) ↔ 1A (II), 1A (I)$_0$ ↔ 1A (II)$_0$, 1A (I)'$_0$ ↔ 1A (II)'$_0$, 1A (I)' ↔ 1A (II)'**, (Figs 3, 7). The calculated chemical shift value of H6 at δ 7.5 of **2** (Table 1) points to the lack of the differences in the spin states of electrons of 2p orbitals of C2 N3, C2 N6, N6 C7.

Table 9. The ^{1}H–NMR chemical shifts δ [ppm] from TMS and the ^{1}H–^{1}H long – range coupling constants [Hz] of **1**

Spectrum No. (CDCl$_3$)	δ	J	NH
4	8.528	$J(H_{11}H_{9A})$ 37.280	
6	8.598	$J(H_{11}H_{9A})$ 38.144	0.1 H
1	7.754	$J(H_{12}H_{9A})$ 38.336	0.43 H
4	8.584	$J(H_{11}H_{9A})$ 38.400	
6	7.852	$J(H_{12}H_{9A})$ 38.912	0.14 H
5	7.998	$J(H_{13}H_{9A})$ 40.064	0.756 H
5	7.974	$J(H_{13}H_{9A})$ 39.296	
4	7.331	$J(H_{14}H_{9A})$ 39.392	0.46 H
4	7.341	$J(H_{14}H_{9A})$ 40.640	
2	6.008	$J(H_8H_{12})$ 39.872	0.071 H
2	5.890	$J(H_8H_{13})$ 41.728	
6	5.839	$J(H_8H_{12})$ 39.936	0.03 H
1	8.152	$J(H_{13}H_{9A})$ 40.672	0.38 H
5	7.819	$J(H_{12}H_{9A})$ 40.832	1.356 H
3	6.012	$J(H_8H_{13})$ 40.832	0.019 H
3	5.895	$J(H_8H_{13})$ 42.368	
3	5.886	$J(H_8H_{14})$ 39.168	
1	8.223	$J(H_{13}H_{9A})$ 41.760	0.38 H
6	7.697	$J(H_{12}H_{9A})$ 41.984	0.14 H
6	8.218	$J(H_{13}H_{9B})$ 42.240	0.172 H
4	8.594	$J(H_{11}H_{9B})$ 42.432	
5	8.223	$J(H_{13}H_{9B})$ 43.776	0.633 H

Table 10. The ^{1}H–NMR chemical shifts δ [ppm] from TMS and the ^{1}H–^{1}H long – range coupling constants [Hz] of **1**

Spectrum No. (CDCl3)	δ	J	NH
1	3.999	$J(H_{7D}H_{11})$ 37.696	0.822 H
6_6	3.999	$J(H_6H_{12})$ 40.960	0.199 H
3	(–0.033)	$J(H_6H_{11})$ 38.272	0.099 H
6_6	4.018	$J(H_6H_{11})$ 38.656	0.19 H
5	5.266	$J(H_{9A}H_{12})$ 40.960	0.9 H
5	5.449	$J(H_{9A}H_{13})$ 39.680	
3	5.477	$J(H_{9A}H_{13})$ 40.192	0.26 H
3	5.787	$J(H_8H_{14})$ 43.136	
4	5.214	$J(H_{9B}H_{14})$ 43.712	0.24 H
4	5.280	$J(H_{9A}H_{12})$ 40.224	

The doublet of a doublet at δ 4.032–4.061 supports the **1A (I) (5, 6)**, **1A (I)'(5, 6), 1A (I)'$_0$ (5, 6), 1A (I)$_0$ (5, 6)** structures (Figs 12, 13, 8).

In ^{15}N NMR spectrum of **1** the chemical shift of N4 δ–22.98[1] points to the pyrrole – type nitrogen atom and to the presence of the polar structures **1A'(1) ↔ 1A (I)'(1) 1A$_0$ (1) ↔ 1A (I)$_0$(1) 1A'$_0$ (1) ↔ 1A (I)'$_0$ (1)** (Fig. 7).

The ^{1}H ^{1}H long-range coupling constants in the 37.280 Hz – 43.776 Hz range[18] support the coupling of the protons of the pyridyl and – N – CH_2–CH = CH_2 groups *via* 2p orbitals of C14 C7 of the rigid structures **A' A'$_a$** and sp^2 hybridization of the exocyclic nitrogen atom N6 (spectra 1–6, Table 9, Fig. 14). The signals at δ – 0.033-5.787 (Table 10, spectra 1, 3–6_6) confirm the transformation of $sp^2 \Leftrightarrow sp^3$ of N6 and **A' ↔ a'**, **A'$_a$ ↔ a'$_a$** resonance structures.

In the ^{1}H NMR spectra $1_{3,\,4}$ (100 MHz, $CDCl_3$) the coupling constants of the protons $J(H_8H_{9B})$ 17.3 Hz, $J(H_8H_{7C})$ 18.9 Hz, $J(H_8H_{7D})$ 11.5 Hz, $J(H_8H_{9A})$ 10.9 Hz [18] confirm the sp^2 hybridization of nitrogen and carbon N6 C7 atoms. The coupling constants of the protons $J(H_8H_{9B})$ 12.3 Hz, $J(H_8H_{9A})$ 8.5 Hz, $J(H_8H_{7C})$ 7.5 Hz, $J(H_8H_{7D})$ 7.4 Hz support the sp^3 hybridization of carbon C7 atom. The coupling constants of the protons $J(H_8H_{7C})$ 8.2 Hz, $J(H_8H_{7D})$ 7.8 Hz[18] confirm the changes of $sp^2 \Leftrightarrow sp^3$ hybridization of the nitrogen and carbon atoms N6 C7.

The ^{1}H ^{1}H long-range coupling constants $J(H_6H_{11})$ 38.272 Hz, $J(H_6H_{11})$ 38.656 Hz (Table 10) support the structures **A'(1) A'(5) A'(6)** (Figs 7, 8).

In the ^{1}H NMR spectra 6_5, 6_6 (100 MHz) of **1** the signals at δ 7.125 and δ 7.120 support the co – existence of two tautomeric forms **A(2, 3) ↔ A(I) (2, 3) ⇒ B(2-4)**, **A(4) ↔ A(I) (4) ⇒ C(3, 4)** and **A(5) ↔ A(I) (5) ⇒ B(5)** or **A(6) ↔ A(I) (6) ⇒ C(6),** respectively. The intensities of the signals at δ 7.125 (2,09H, Fig. 15) and δ 7.120 (3.03H, Fig. 15) indicate the interconvertion of **1A(2) ↔ 1 A(I) (2) ⇒ 1B(2, 4)**, **1A(3) ↔ 1A(I) (3) ⇒ 1B(3, 4),**

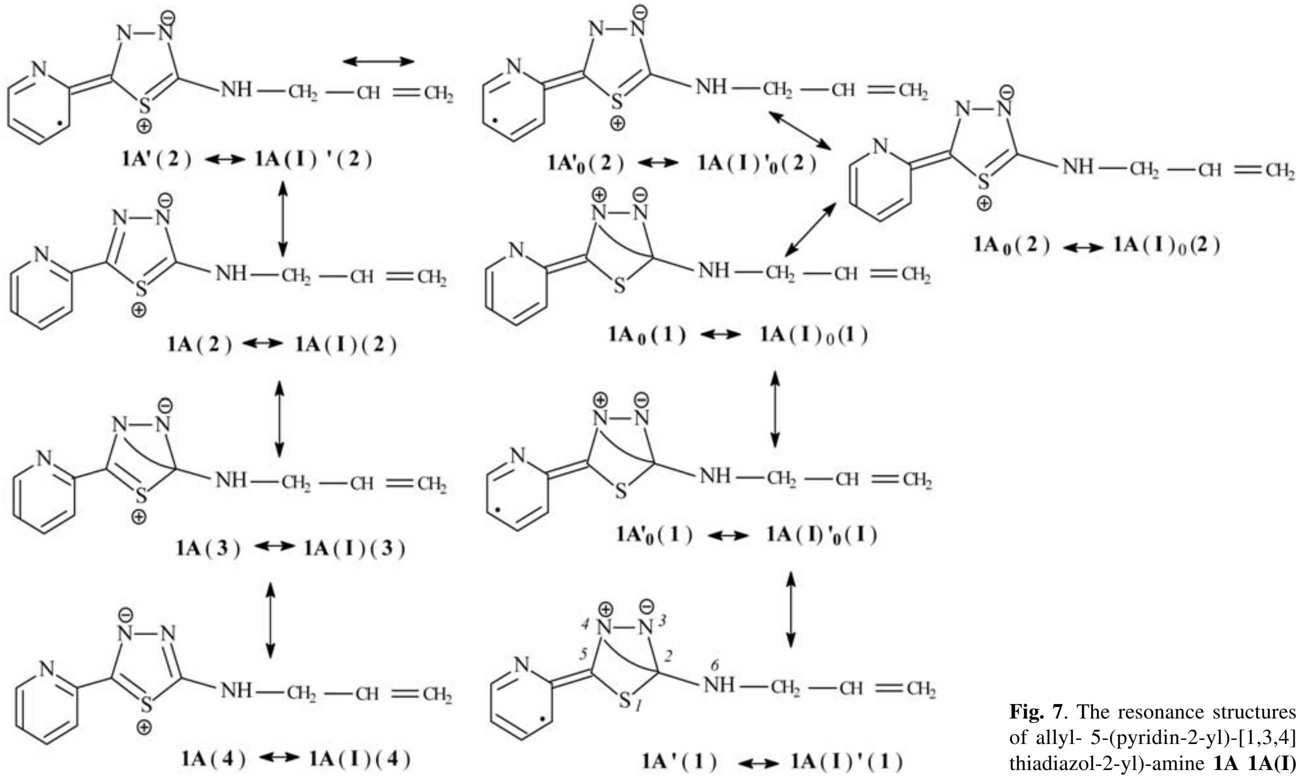


Fig. 7. The resonance structures of allyl- 5-(pyridin-2-yl)-[1,3,4] thiadiazol-2-yl)-amine **1A 1A(I) 1A' 1A(I)'**.

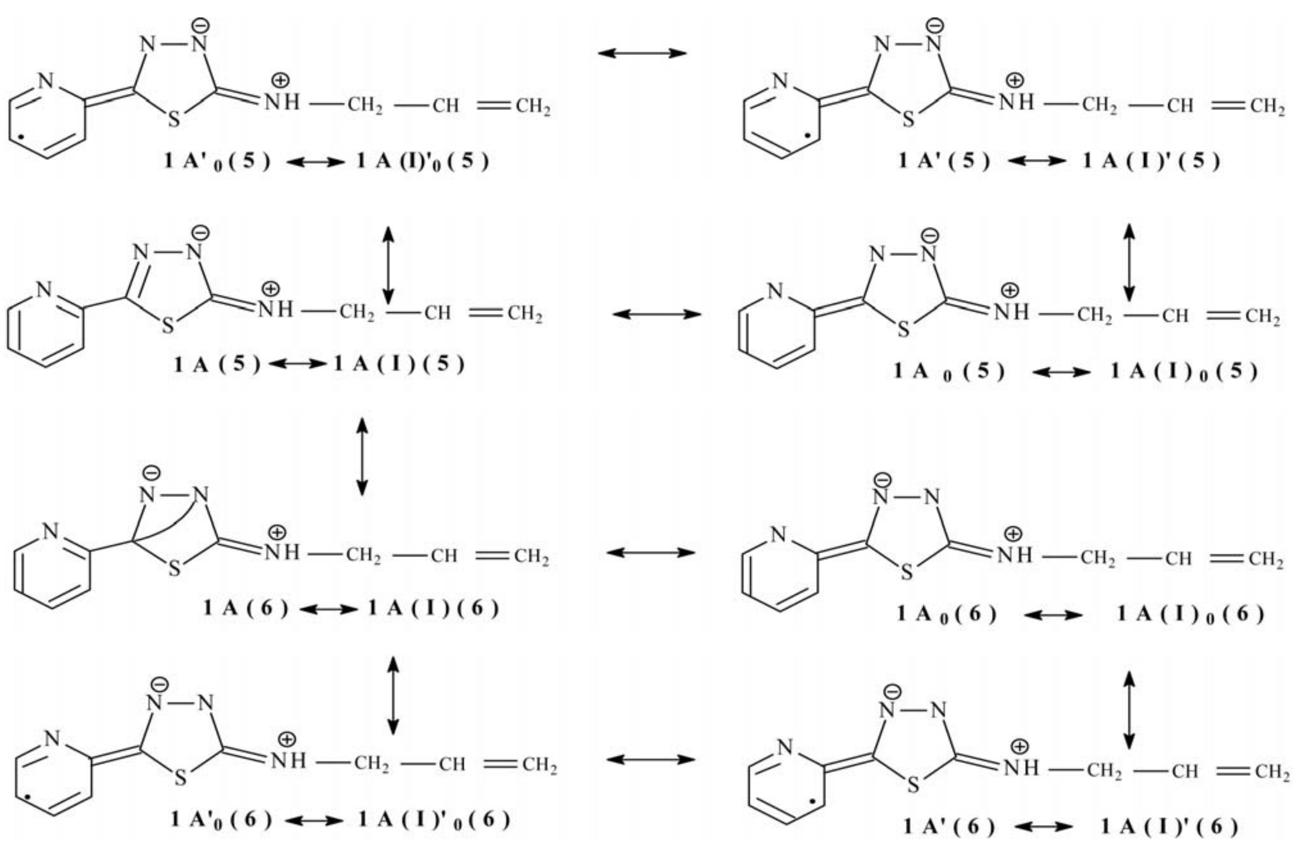


Fig. 8. The resonance structures of allyl-(5-(pyridin-2-yl)-[1,3,4] thiadiazol-2-yl)-amine **1A 1A' 1A (I) 1A(I)'**

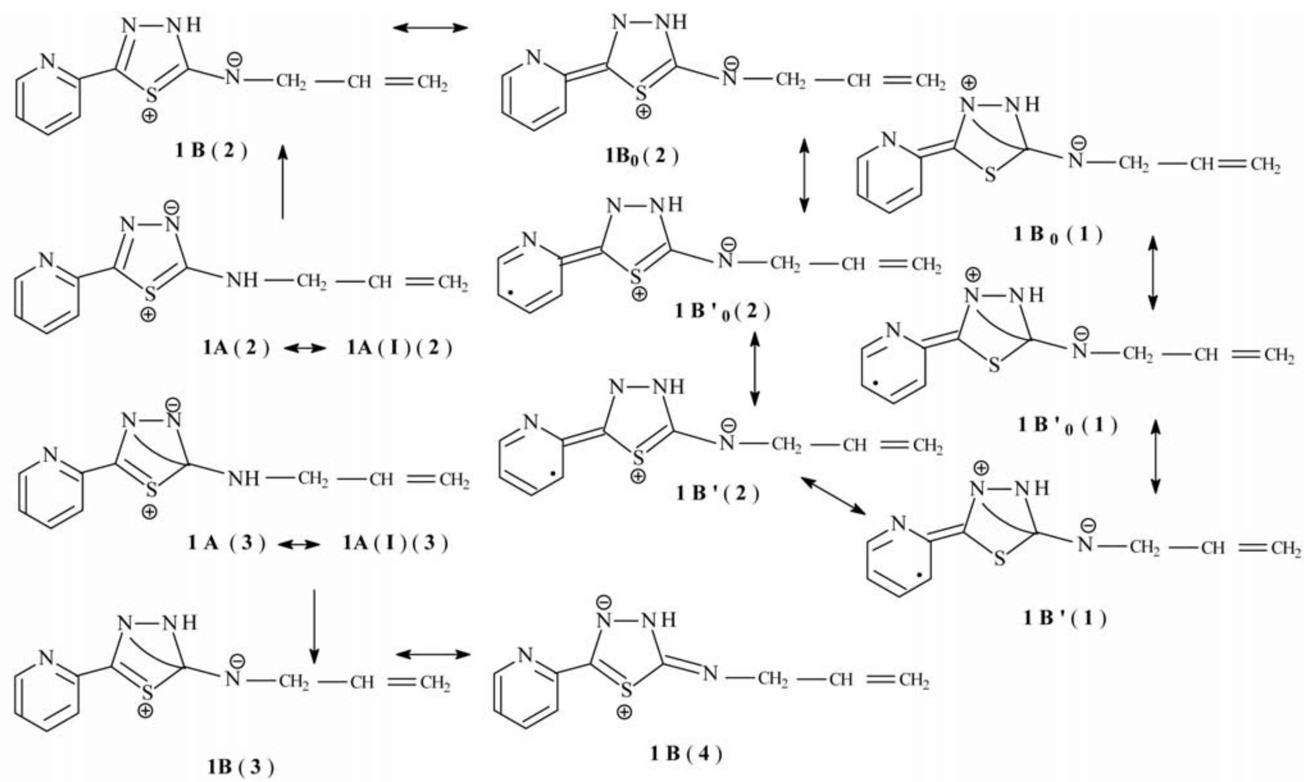


Fig. 9. The tautomeric interconvertions of **1A** ↔ **1A(I)** ⇒ **1B** tautomers.

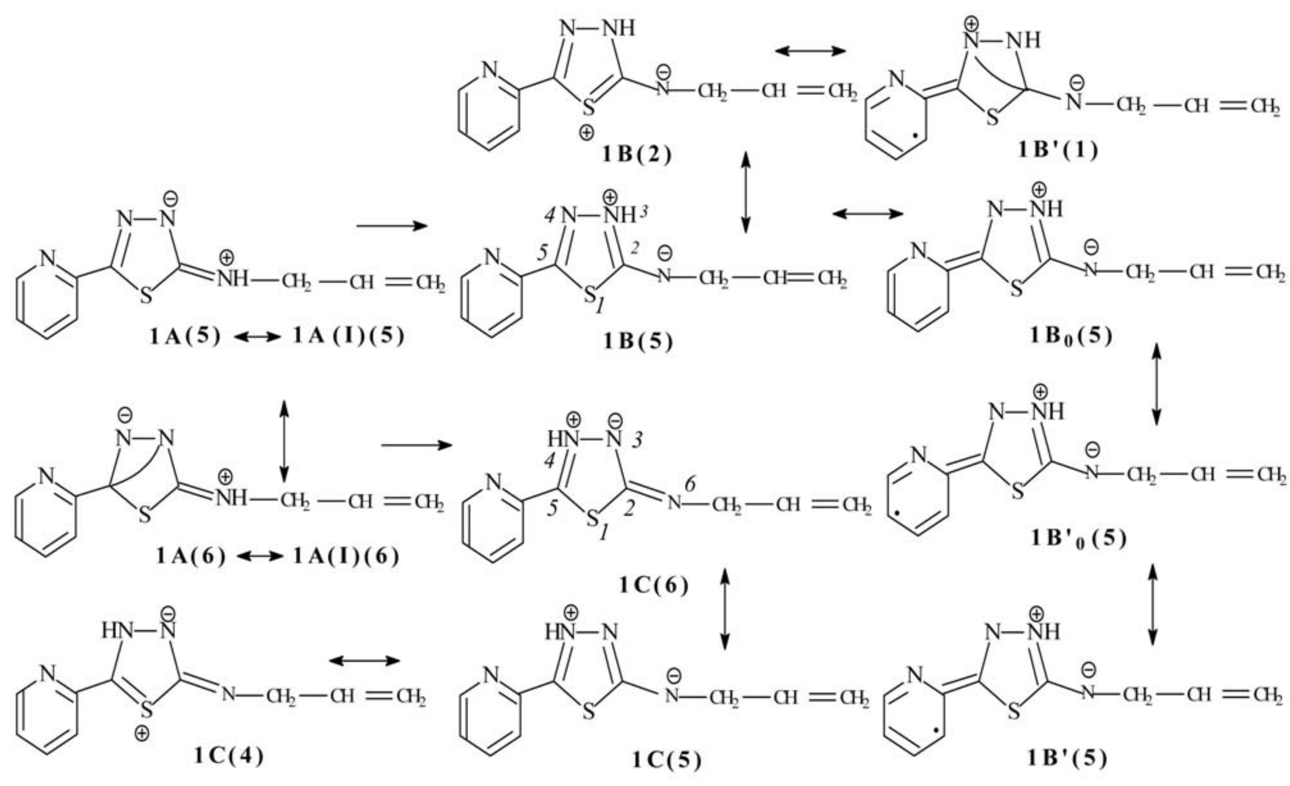


Fig. 10. The tautomeric transitions of **1A** ↔ **1A(I)** ⇒ **1B** and **1A** ↔ **1A(I)** ⇒ **1C** tautomers

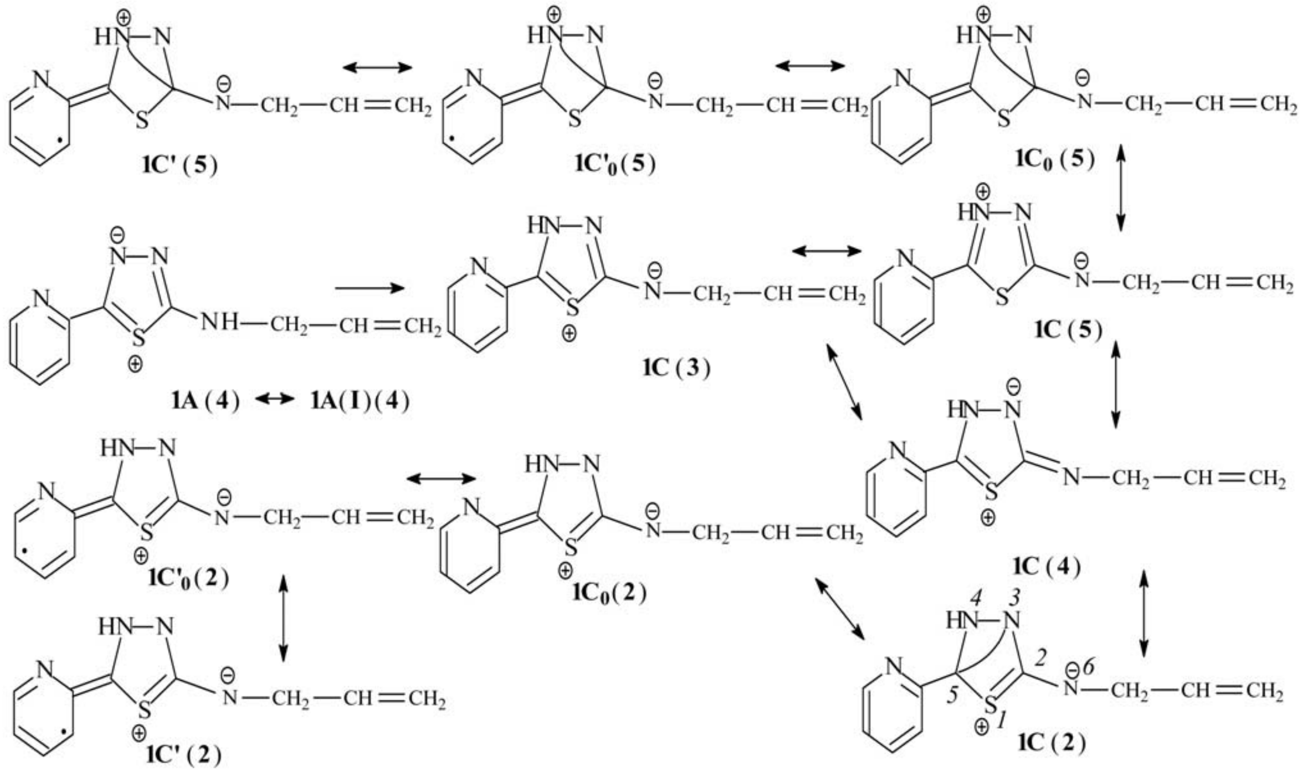


Fig. 11. The tautomeric balance of **1A ↔ 1A(I) ⇒ 1C** tautomers

Fig. 12. The [1]H NMR signals of H 7 proton at δ 3.922–4.061 (spectrum 1_1, DMSO, 100 MHz)

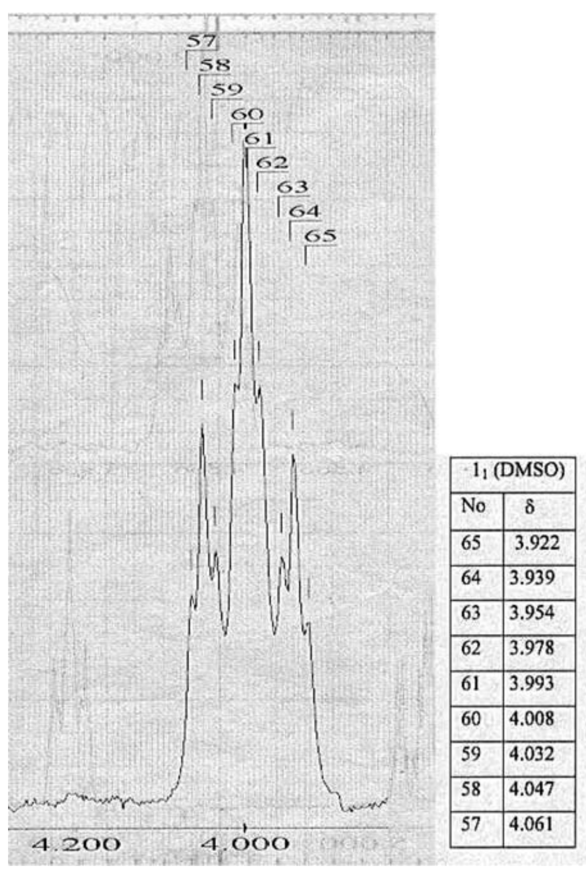
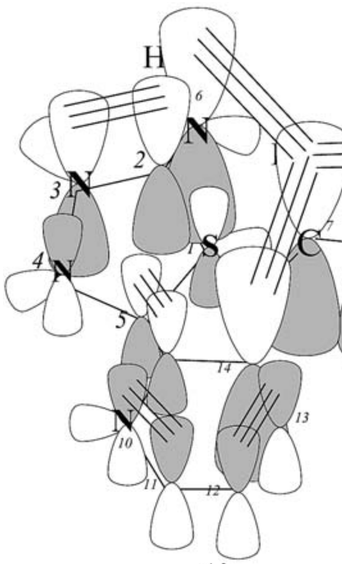
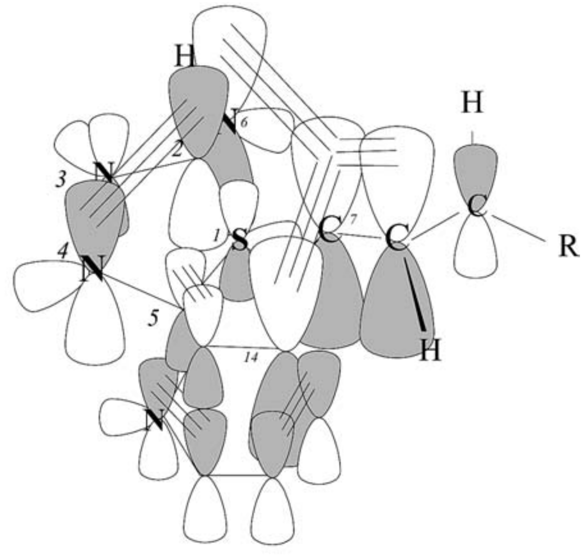


Fig. 13. The [1]H NMR signals of H 7 proton at δ 3.922–4.061 (spectrum 1_1, DMSO, 100 MHz)



A'

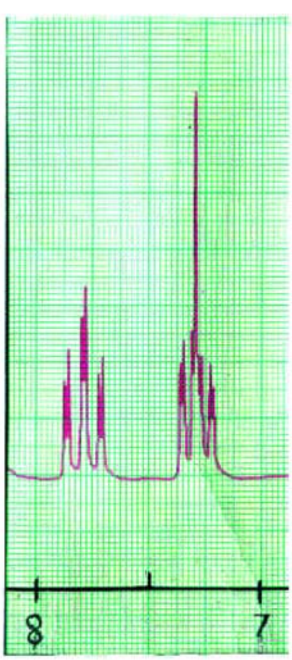


A'$_a$

Fig. 14. The resonance rigid structures **A'**, **A'$_a$** of allyl-(5-pyridin-2-yl-[1,3,4] thiadiazol-2-yl)-amine

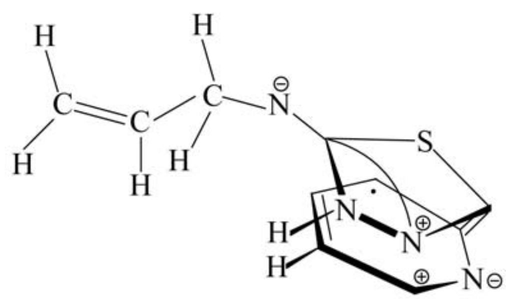
1A(4) ↔ 1 A(I) (4) ⇒ 1C(3, 4) and **1A(5) ↔ 1A(I) (5) ⇒1B (5)** or **1A(6) ↔ 1A(I) (6) ⇒ 1C(6)** tautomers, respectively (Figs 9–11, Table 8).

The signals at δ 7.040 (0.786H) and δ 7.035 (0.802H) correspond to the NH proton of the structures **1A (2, 3, 4)$_5$ ↔ 1A (I) (2, 3, 4)$_5$, 1B (2, 3, 4)$_5$ 1C (2, 3, 4)$_5$,** and **1A (5)$_5$ ↔ 1A (I) (5)$_5$, 1A (6)$_5$ ↔ 1A (I) (6)$_5$, 1B (5)$_5$ 1C (6)$_5$ 1C (5)$_5$**, respectively (Figs 9–11, 4, spectra 6_5, 6_6, Table 8).

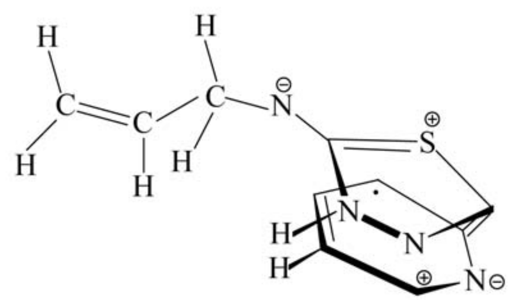


Spectrum No	ppm	integral
6_5	7.125	1H 658.176 1376.512
6_6	7.120	1H 400.896 1213.696

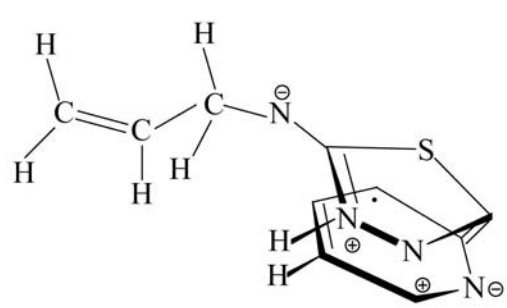
Fig. 15. The [1]H NMR signals of NH proton at δ 7.125, δ 7.120 (spectra 6_5, 6_6)



1B'(1)$_2$

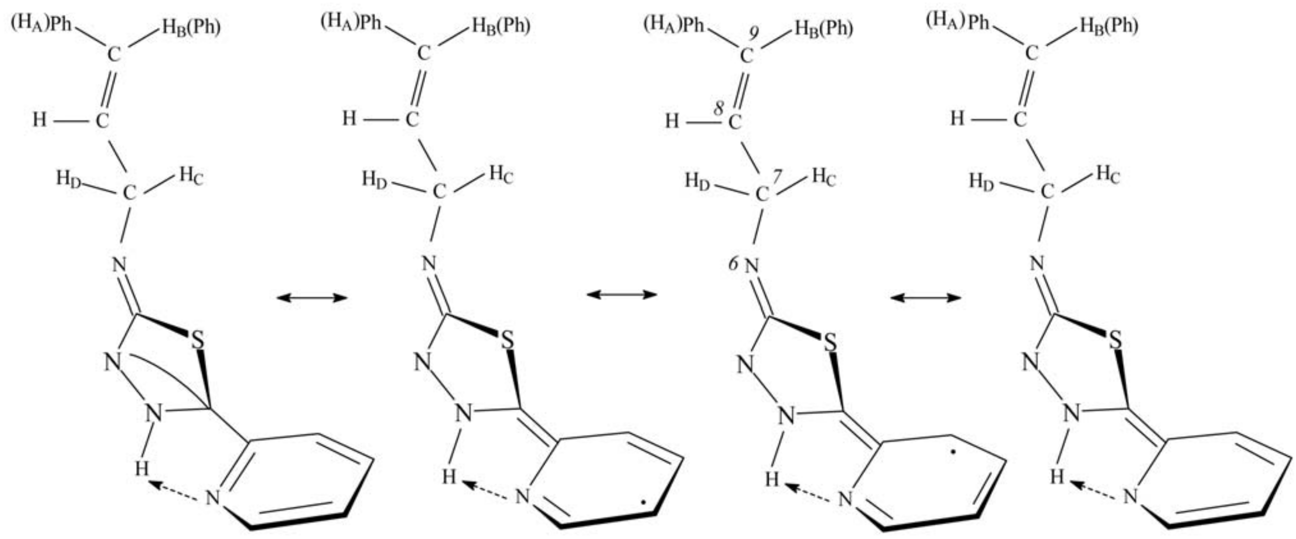


1B'(2)$_2$



1B'(5)$_2$

Fig. 16. The resonance structures of 3H allyl-(5-pyridin-2-yl-[1,3,4] thiadiazol-2-ylidene)-amine **1B'**



2C 2C(II) **2C'₀ 2C(I)'₀ 2C(II)'₀** **2C' 2C(I)' 2C(II)'** **2C₀ 2C(I)₀ 2C(II)₀**

Fig. 17. The resonance structures 4H-(3-phenyl-allyl)-(5-pyridin-2-yl-[1,3,4] thiadiazol-2-ylidene) amine **2C**, **2C'**.

Table 11. The ^{1}H–NMR chemical shifts δ [ppm] from TMS of the NH group of tautomers **1A 1A'**.

Spectrum No, Solvent	δ	NH	Structure
1_1 (DMSO)	8.637 – 8.562	0.08 H	**1A 1A'**
1_3 ($CDCl_3$)	8.606 – 8.530	0.2 H	**$1A_1$ $1A_2$**
1_4 ($CDCl_3$)	8.601 – 8.525	0.05 H	
3 ($CDCl_3$)	8.598 – 8.537	0.23 H	
6 ($CDCl_3$)	8.598 – 8.523	0.1 H	
1 ($CDCl_3$)	8.594 – 8.519	0.38 H	
5 ($CDCl_3$)	8.589 – 8.514	0.637 H	
2 ($CDCl_3$)	8.580 – 8.537	0.08 H	
5($CDCl_3$)	8.077 – 7.974	0.756 H	**$1A'_1$**
4($CDCl_3$)	7.852 – 7.683	0.13 H	**$1A'_2$**
6($CDCl_3$)	7.852 – 7.678	0.14 H	**$1A'_3$**
1($CDCl_3$)	7.847 – 7.674	0.43 H	
2($CDCl_3$)	7.847 – 7.674	0.18 H	
3($CDCl_3$)	7.847 – 7.674	0.25 H	
5($CDCl_3$)	7.838 – 7.646	1.356 H	
1_7($CDCl_3$)	7.78 – 7.73	0.505 H	

In the 2D ^{1}H ^{1}H COSY correlation spectrum the cross – peak between H3 at δ 6.750 and H12 at δ 7.8 supports **B'(1, 2, 5)$_2$** structures of **b –** type tautomer of **1** (Fig. 16, Table 8). In the ^{1}H–NMR spectrum 8_5 of product **2** recorded in $CDCl_3$ solution at 100 MHz the considerable deshielding of the NH proton at δ 13.64[22] indicates the possible intramolecular hydrogen bond and supports **2C' 2C (I)' 2C (II)'** tautomers (Fig. 17).

In the ^{1}H NMR spectrum 1_1 (100 MHz, DMSO) of **1** the magnitude of the couplings $J(H_8H_{7D}) = J(H_8H_{7C})$ 8.2 Hz[18] support the changes of $sp^2 \Leftrightarrow sp^3$ hybridization of the nitrogen and carbon atoms N6 C7. The coupling constants of the protons $J(H_8H_{9B})$ 15.4 Hz, $J(H_8H_{9A})$ 8.5 Hz, $J(H_8H_{7C})$ 7.6 Hz, $J(H_8H_{7D})$ 7.6 Hz[18] support the sp^3 hybridization of C7 carbon atom.

In the ^{1}H-NMR (100 MHz) spectra of **1** the NH proton signals in the δ 8.637–8.514 and δ 8.077–7.646 range confirm the **1A**, **1A'**, **$1A_1$**, **$1A_2$** and **$1A'_1$**, **$1A'_2$ $1A'_3$** resonance structures, respectively (Table 11).[2] The signals at δ 8.594 $J(H_{11}H_{9B})$ 42.432 Hz , δ 8.584 $J(H_{11}H_{9A})$ 38.400 Hz, δ 8.528 $J(H_{11}H_{9A})$ 37.280 Hz and δ 7.998 $J(H_{13}H_{9A})$ 40.064 Hz (spectra 4, 5 Table 9)[2] point to the transition of **A'↔ A** and **A'_1 ↔ A_1** tautomers as well as to the rapid exchange at the NH group hydrogen of structures **A A'**.

The interconvertions of the structures **1A ↔ 1A' ↔ $1A'_a$, 1A (I) ↔ 1A (I)' ↔ 1A (I)'$_a$** and the rapid exchange of the NH hydrogen suggest the proton transfer of **1A ↔ 1A (I) ⇒ 1B, 1A ↔ 1A (I) ⇒ 1C** tautomers *via* solvent. Doubled signals of the protons corresponding to both tautomeric forms are present in the ^{1}H-NMR (100 MHz) spectra of **1** (Fig. 15, Table 8). The proton transfer reactions for different systems have been described in the literature.[23, 24]

In the ^{1}H NMR (100 MHz) spectra 1_4, 1–6 the NH proton singlets in the δ 6.771 to 6.500 range with the intensity of 1H confirm the resonance structures **1A'(1, 2) ↔ 1A (I)'(1, 2), 1A'(5) ↔ 1A (I)'(5), 1A'(6) ↔ 1A (I)'(6), 1B'(1, 2, 5), 1C'(2, 5)** (Table 8, Figs 7–11, 4).

4. Conclusions

The ^{1}H, ^{13}C, ^{15}N NMR studies (100 MHz) of allyl (5-pyridin-2-yl-[1,3,4] thiadiazol-2-yl-) amine support the

A ↔ **A'** ↔ **A'$_a$, A(I)** ↔ **A(I)'** ↔ **A(I)'$_a$** structures. The intensities of the signals of N-H proton at δ 7.125 and δ 7.120 confirm the balance of two tautomeric forms **A** ↔ **A (I)** ⇒ **B, A** ↔ **A (I)** ⇒ **C** in the solution. Doubled signals of the NH proton in the ^{1}H-NMR (100 MHz) spectra of **1** (Fig. 15, Table 8) confirm both tautomeric forms. Because of the rapid exchange of NH group hydrogen in this case the pathway of the proton transfer *via* solvent may take place.

The signals of H7 in the ^{1}H NMR spectrum 1_1 (100 MHz, DMSO) of **1** at δ 3.922–3.954, δ 3.978–4.008, δ 4.032–4.061, the coupling constants of the protons of allyl-substituent as well as the calculated chemical shift of the nitrogen atom N6 δ – 131.57 confirm **1A 1A' 1A'$_a$ 1A (I) 1A (I)' 1A (I)'$_a$** and **1B 1B', 1C 1C'** tautomers.

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Povzetek

Radikalske in ionske strukture alil-(5-piridin-2-il-[1,3,4]tiadiazol-2-il)-amina 1A ↔ 1A' ↔ 1A'$_a$, 1A (I) ↔ 1A (I)' ↔ 1A (I)'$_a$ so bile določene z uporabo ^{1}H (100 MHz, 500 MHz) ^{13}C and ^{15}N NMR spektroskopije in B3LYP/6-31G** računi. Spekter ^{1}H NMR (100 Mhz) nam je potrdil obstoj tavtomernega prehoda 1A ↔ 1A (I) ⇒ 1B, 1A ↔ 1A (I) ⇒ 1C.