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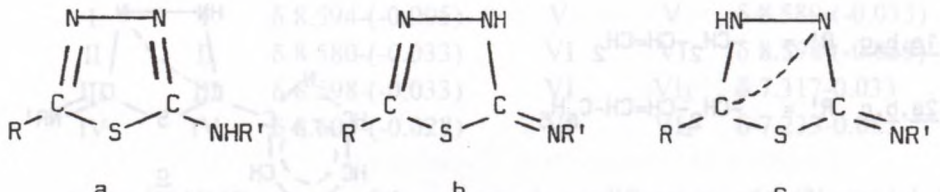
Tautomerism of 1,3,4-thiadiazole. Part I

Tautomeria 1,3,4-tiadiazolu. I

INTRODUCTION

Theoretically 5R-2R'-amino-1,3,4-thiadiazole system a) may exist in its tautomeric modifications of 3H-5R-2R'-imino-1,3,4-thiadiazole b) and 3H-2R-5R'-imino-1,3,4-thiadiazole c), (Scheme 1).

Scheme 1.



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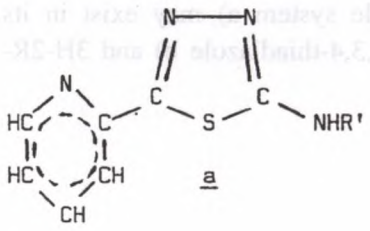
G. Kornis has reported [1] about the presence of the amino and imino forms a), b) of 2-amino-1,3,4-thiadiazoles and that the tautomeric equilibrium is influenced by the substituents both at the exocyclic nitrogen atom and in the 5-position of 1,3,4-thiadiazole ring.

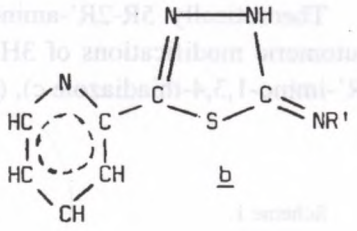
During the studies on the ^{1}H NMR spectra of 5-substituted-2-cinnamylamino-1,3,4-thiadiazole [2], a signal of NH group at various chemical shifts has been observed. This fact may suggest the differences in the structure of 5-substituted-2-cinnamylamino-1,3,4-thiadiazole . These data induced us to examine the structure of 5-substituted-2 -cinnamylamino-1,3,4-thiadiazole more exactly. There are no reports on this subject in the literature.

RESULTS AND DISCUSSION

The aim of the present paper was to describe the structure of 5-(2'-pyridyl-)-2-allyl-(cinnamyl-)amino-1,3,4-thiadiazole a) and its tautomeric modifications b), c) (Scheme 2).

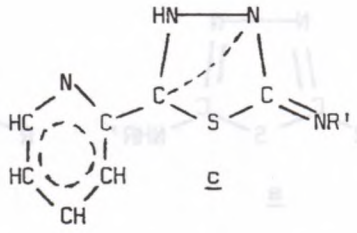
Scheme 2.





1a,b,c R' = $-CH_2-CH=CH_2$

2a,b,c R' = $-CH_2-CH=CH-C_6H_5$



The tautomeric modifications of 5-(2'-pyridyl-)2-allylamino-1,3,4-thiadiazole 1a), 1b), 1c) were obtained by the cyclization of N^1-(allyl-thiocarbamyl-)-N^3-phenyl-2-picolineamidrazone (methods I–IV) with:

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 N^3-phenyl-2-picolineamidrazone dihydrochloride and allylisothiocyanate (methods V,VI) in:

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

The tautomeric forms of 5-(2'-pyridyl-)-2-cinnamylamino-1,3,4-thiadiazole 2a), 2b), 2c) were obtained by the cyclization of N^1-(cinnamyl-thiocarbamyl-)N^3-phenyl-2-picolineamidrazone [2] (methods VII; VIII) with:

VII. boiling diluted 3,6% hydrochloric acid
VIII. concentrated 36% hydrochloric acid at room temperature

or by condensation of N^3-phenyl-2-picolineamidrazone dihydrochloride and cinnamylisothiocyanate [2] (methods IX, X) in:

IX. boiling anhydrous ethanol
X. boiling N,N-dimethylformamide.

In the ^{1}H NMR spectra of the tautomeric modifications of 5-(2'-pyridyl-)-2-allylamino-1,3,4-thiadiazole 1a), 1b), 1c) the chemical shifts of the signals were ranged as follows:

method	spectrum No		method	spectrum No	
I	I	δ 8.594-(-0.005)	V	V	δ 8.589-(-0.033)
II	II	δ 8.580-(-0.033)	VI	VI	δ 8.598-(-0.033)
III	III	δ 8.598-(-0.033)	VI	VI_3	δ 7.317-0.033
IV	IV	δ 8.603-(-0.028)	VI	VI_4	δ 7.233-0.033

In the ^{1}H NMR spectra of the tautomeric modifications of 5-(2'-pyridyl-)2-cinnamylamino-1,3,4-thiadiazole 2a), 2b), 2c) the chemical shifts of the signals were ranged as follows:

method	spectrum No		method	spectrum No	
VII	VII	δ 8.580-0.042	IX	IX	δ 8.570-(-0.033)
VIII	VIII	δ 8.547-0.019	X	X	δ 8.570-(-0.005)
VIII	$VIII_5$	δ 13.64-0.000			

In the ^{1}H NMR spectra of products 1a), 1b), 1c), 2a), 2b), 2c) obtained by the methods I–X, spectra I–X, VII_5 the signals of the protons of allyl, cinnamyl, pyridyl substituents as well as of NH group of 1,3,4-thiadiazole have been recorded. In the ^{1}H NMR spectra of products 1a), 1b), 1c) obtained by the methods VI, spectra VI_3, VI_4 the signals of NH group of 1,3,4-thiadiazole ring have only been recorded.

The ^{1}H NMR spectra of products 1a), 1b), 1c), 2a), 2b), 2c) contain signals confirming the presence of unsaturated groups $-CH_2-CH=CH_2$, $-CH_2-CH=CH-$ $-C_6H_5$ as well as of the pyridyl substituent (Tables 1, 3). In the ^{1}H NMR spectrum of products 1a), 1b), 1c) obtained by the method V, spectrum V there are present double signals of α(6'H) γ(4'H) β(5'H) β(3'H) proton and suggest the presence of the following mesomeric structures of the pyridine ring, Scheme 3.

In the ^{1}H NMR spectra of compounds 1abc), 2abc) obtained by the methods I–X there appear the signals of the protons H_c H_d of allyl-(cinnamyl-) substituents at various chemical shifts values and support the presence of the structures $1a_{de}$ $1b_{de}$ $1c_{de}$, $2a_{fg}$ $2b_{fg}$ $2c_{fg}$, Schemes 4, 5, respectively.

The chemical shifts values of the protons H_c H_d are ranged as follows:

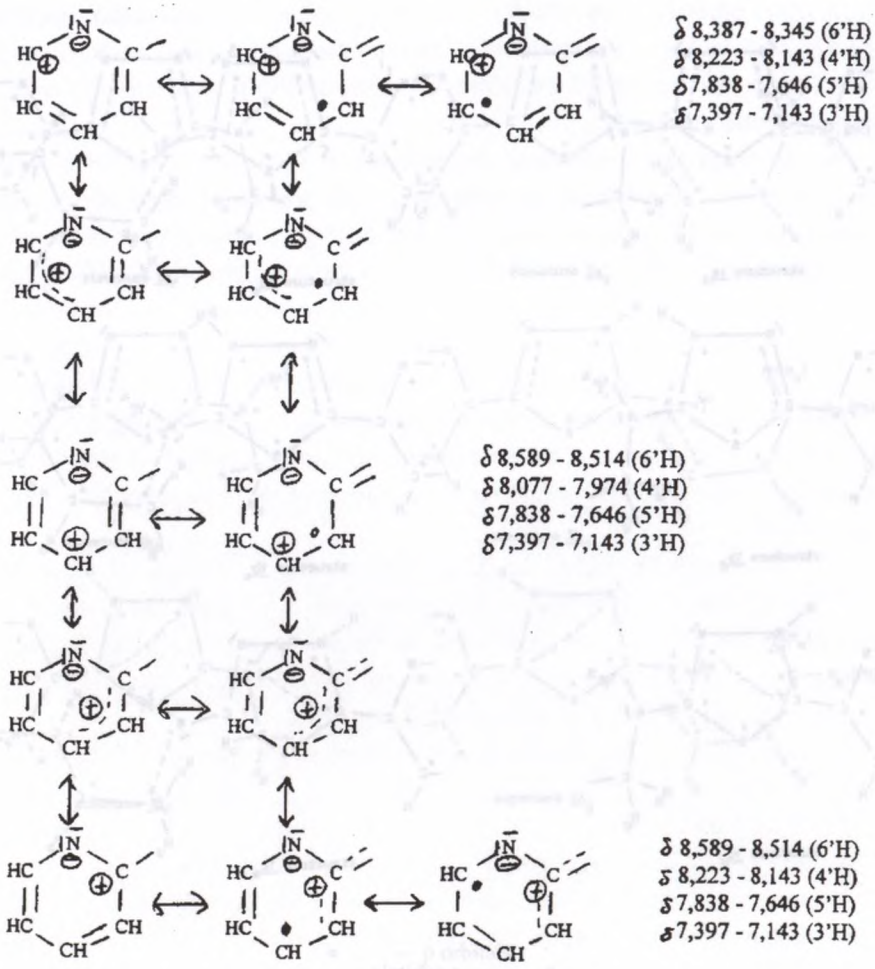
δ 3.999–4.079 (method I, spectrum I)
δ 4.003–4.083 (method II,VI, spectra II,VI)
δ 4.003–4.088 (method III,IV, spectra III,IV)
δ 4.003–4.088 (method V, spectrum V)

$1a_{de}1b_{de}1c_{de}$

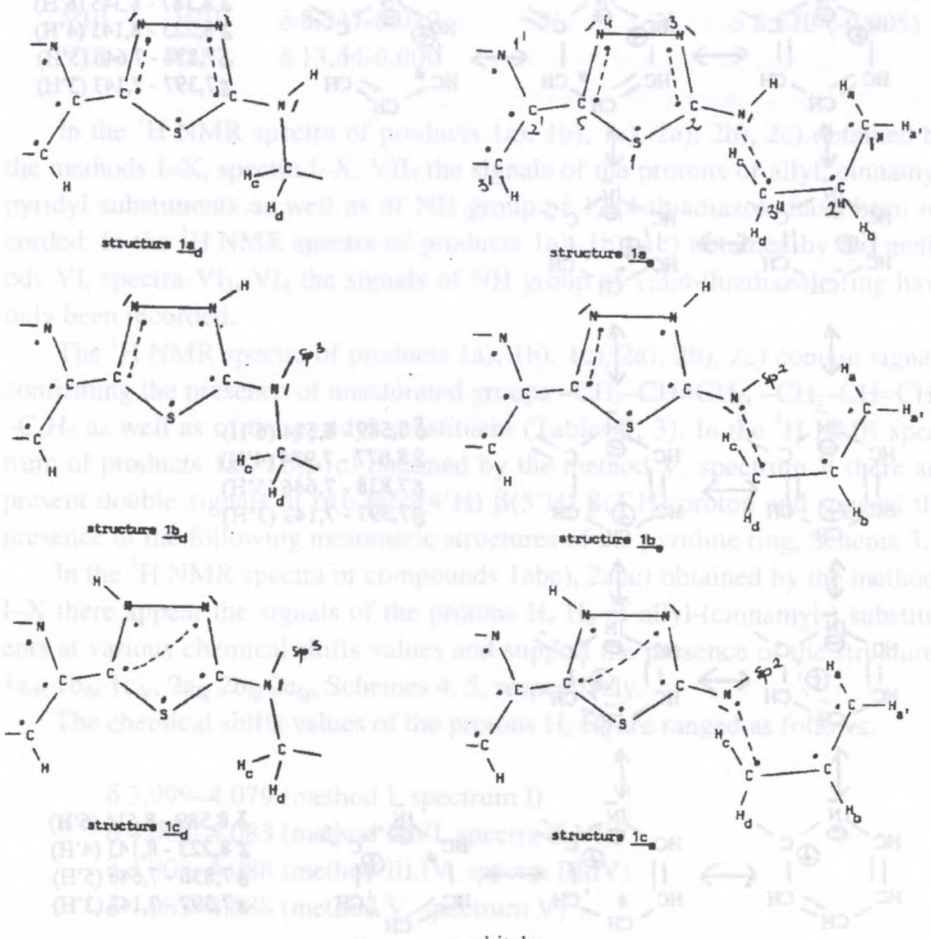
δ 4.163–4.224 (method VIII, spectrum VIII)
δ 4.182–4.252 (method IX, spectrum IX)
δ 4.196–4.257 (method X, spectrum X)
δ 4.210–4.266 (method VII, spectrum VII)

$2a_{fg}2b_{fg}2c_{fg}$

Scheme 3.


δ 8,387 - 8,345 (6'H)
δ 8,223 - 8,143 (4'H)
δ 7,838 - 7,646 (5'H)
δ 7,397 - 7,143 (3'H)
δ 8,589 - 8,514 (6'H)
δ 8,077 - 7,974 (4'H)
δ 7,838 - 7,646 (5'H)
δ 7,397 - 7,143 (3'H)
δ 8,589 - 8,514 (6'H)
δ 8,223 - 8,143 (4'H)
δ 7,838 - 7,646 (5'H)
δ 7,397 - 7,143 (3'H)
• – p orbitals
| – electron pair
⊖ – negative charge
⊕ – positive charge

Scheme 4.

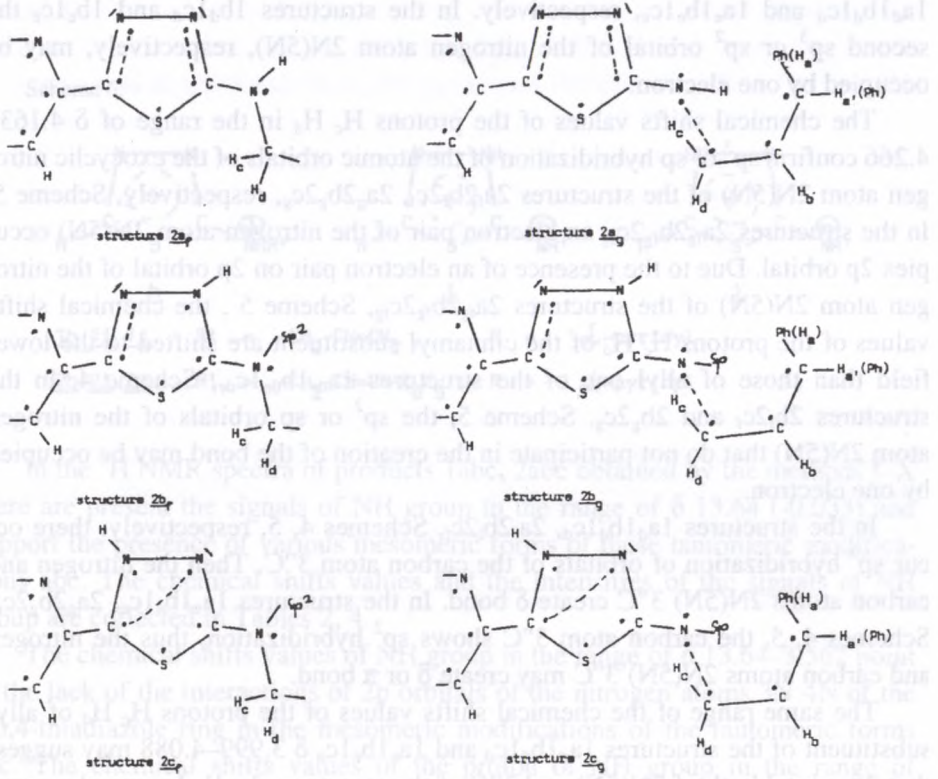


• – p orbitals

| – electron pair

sp^2, sp^3 – orbitals

Scheme 5.



• – p orbitals

| – electron pair

sp, sp^2 – orbitals

The chemical shifts values of the protons H_c H_d of allyl and cinnamyl substituents of the structures $1a_{de}1b_{de}1c_{de}$, $2a_{fg}2b_{fg}2c_{fg}$, Schemes 4, 5, in the range of δ 3.999–4.088 and δ 4.163–4.266, respectively, point to the differences in the hybridization of the atomic orbitals of the exocyclic nitrogen atom 2N(5N) of 1,3,4-thiadiazole ring.

The chemical shifts values of the protons H_c H_d in the range of δ 3.999–4.088 support sp^3 or sp^2 hybridization of the nitrogen atom 2N(5N) of the structures $1a_d1b_d1c_d$ and $1a_e1b_e1c_e$, respectively, Scheme 4. An electron pair of the exocyclic nitrogen atom 2N(5N) occupy sp^3 or sp^2 orbital of the structures $1a_d1b_d1c_d$ and $1a_e1b_e1c_e$, respectively. In the structures $1b_d1c_d$ and $1b_e1c_e$ the second sp^3 or sp^2 orbital of the nitrogen atom 2N(5N), respectively, may be occupied by one electron.

The chemical shifts values of the protons H_c H_d in the range of δ 4.163–4.266 confirm sp^2 or sp hybridization of the atomic orbitals of the exocyclic nitrogen atom 2N(5N) of the structures $2a_f2b_f2c_f$, $2a_g2b_g2c_g$, respectively, Scheme 5. In the structures $2a_{fg}2b_{fg}2c_{fg}$ an electron pair of the nitrogen atom 2N(5N) occupies 2p orbital. Due to the presence of an electron pair on 2p orbital of the nitrogen atom 2N(5N) of the structures $2a_{fg}2b_{fg}2c_{fg}$, Scheme 5 , the chemical shifts values of the protons H_c H_d of the cinnamyl substituent are shifted to the lower field than those of allyl one of the structures $1a_{de}1b_{de}1c_{de}$, Scheme 4. In the structures $2b_f2c_f$ and $2b_g2c_g$, Scheme 5, the sp^2 or sp orbitals of the nitrogen atom 2N(5N) that do not participate in the creation of the bond may be occupied by one electron.

In the structures $1a_d1b_d1c_d$, $2a_f2b_f2c_f$, Schemes 4, 5, respectively, there occur sp^3 hybridization of orbitals of the carbon atom 3"C. Then the nitrogen and carbon atoms 2N(5N) 3"C create δ bond. In the structures $1a_e1b_e1c_e$, $2a_g2b_g2c_g$, Schemes 4, 5, the carbon atom 3"C shows sp^2 hybridization, thus the nitrogen and carbon atoms 2N(5N) 3"C may create δ or π bond.

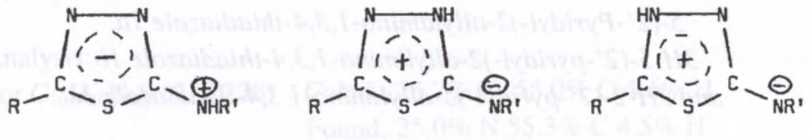
The same range of the chemical shifts values of the protons H_c H_d of allyl substituent of the structures $1a_d1b_d1c_d$ and $1a_e1b_e1c_e$ δ 3.999–4.088 may suggest that 2p orbital both of 2N(5N) and 3"C of the structures $1a_e1b_e1c_e$ may be occupied by one electron and may create δ or π bonds between these atoms.

The analogous values of the chemical shifts of the protons H_c H_d of cinnamyl substituent of the structures $2a_f2b_f2c_f$ and $2a_g2b_g2c_g$ δ 4.163–4.266 point that one of 2p orbitals of 2N(5N) of the structures $2a_g2b_g2c_g$ is occupied by an electron pair. The second 2p orbital of 2N(5N) and 2p orbital of 3"C, each of them occupied by one electron, may create δ or π bond between these atoms. The small differences in the chemical shifts values of the protons H_c H_d of allyl, cinnamyl substituents of the structures both $1a_{de}1b_{de}1c_{de}$ and $2a_{fg}2b_{fg}2c_{fg}$ suggest the differences in the polarization of the bond of the nitrogen and carbon atoms 2N(5N) 3"C.

Since exocyclic nitrogen atom 2N(5N) of 1,3,4-thiadiazole ring may show sp^3, sp^2 or sp hybridization then the nitrogen and carbon atoms 2N(5N), 2C(5C)

may create single or double bonds. Due to the possible interactions of 2p orbitals of 2C(5C), 2N(5N) in the molecules of the studied systems $1a_e2a_{fg}1b_e2b_{fg}1c_e2c_{fg}$ one can expect the mesoionic forms 1h 2h, 1i 2i, 1j 2j, respectively, Scheme 6.

Scheme 6.



h i j

1h 1i 1j R' = $-CH_2-CH=CH_2$, R = 4-pyridyl

2h 2i 2j R' = $-CH_2-CH=CH-C_6H_5$, R = 4-pyridyl

In the ^{1}H NMR spectra of products 1abc, 2abc obtained by the methods I–X there are present the signals of NH group in the range of δ 13.64 (-0.033) and support the presence of various mesomeric forms of these tautomeric modifications abc. The chemical shifts values and the intensities of the signals of NH group are collected in Tables 2, 4.

The chemical shifts values of NH group in the range of δ 13.64–3.562 point to the lack of the interactions of 2p orbitals of the nitrogen atoms 3N 4N of the 1,3,4-thiadiazole ring in the mesomeric modifications of the tautomeric forms abc. The chemical shifts values of the proton of NH group in the range of δ 3.412 (-0.033) suggest the presence of the interactions of 2p orbitals of the nitrogen atoms 3N 4N of the 1,3,4-thiadiazole ring in the mesomeric forms of the tautomeric structures abc.

EXPERIMENTAL

The ^{1}H NMR spectra were measured with a Tesla BS 677A spectrometer (100MHz with T.F.) in $CDCl_3$ at room temperature with TMS as the internal standard. Chemical shifts are given in the δ scale. Melting points were uncorrected.

N^1-(Allyl-thiocarbamyl-)-N^3-phenyl-2-picolineamidrazone was the new compound. It was obtained by means of a method previously described [3]. M.p. 145–147 °C (EtOH, 70.9% yield).

Analysis:
For $C_{16}H_{17}N_5S$ (311.402) Calcd.: 22.5% N, 61.8% C, 5.5% H
Found.: 21.8% N, 61.6% C, 5,0% H

5-(2'-Pyridyl-)2-allylamino-1,3,4-thiadiazole 1a, 3H-5-(2'-pyridyl-)2-allylimino-1,3,4-thiadiazole 1b and 3H-2-(2'-pyridyl-)5-allylimino-1,3,4-thiadiazole 1c

Method I

5mmole of N^1-(allyl-thiocarbamyl-)N^3-phenyl-2-picolineamidrazone in 10mmole of 3.6% ethanolic solution of HCl was left for 48 hrs at room temperature. The solvent was removed. The crude residue was boiled with 100cm^3 of 4% NaOH. The insoluble product was filtered off, washed with water and crystallized from ethanol-water mixture. M.P. 156–158 °C, 1.0g (91.7% yield).

Analysis:
For $C_{10}H_{10}N_4S$ (218.278) Calcd.: 25.7% N
Found.: 25.3% N

Method II

5mmole of N^1-(allyl-thiocarbamyl-)N^3-phenyl-2-picolineamidrazone in 10mmole of 3.6% hydrochloric acid was left for 48 hrs at room temperature. The reaction mixture was poured into 15cm^3 of water and neutralized with an aqueous ammonia. The crude product was filtered and boiled with 100cm^3 of 4% NaOH. The precipitate was filtered off, washed with water and crystallized from ethanol-water. M.p. 158–160 °C, 1.0g (91.7% yield).

Analysis:
For $C_{10}H_{10}N_4S$ (218.278) Calcd.: 25.7% N
Found: 24.8% N

Method III

5mmole of N^1-(allyl-thiocarbamyl-)N3-phenyl-2-picolineamidrazone in 25cm^3 (0.25mole) of 36% hydrochloric acid was left for 48hrs at room temperature. The reaction mixture was poured into 50cm^3 of water and neutralized with an aqueous ammonia. The precipitate was filtered off, washed with water and crystallized from water. M.p. 156–157 °C, 1.0g (91.7% yield).

Analysis:
For $C_{10}H_{10}N_4S$ (218.278) Calcd.: 25.7% N, 55.0% C 4.6% H
Found: 25.0% N 55.3% C 4.5% H

Method IV

5mmole of N^1-(allyl-thiocarbamyl-)N^3-phenyl-2-picolineamidrazone in 25cm^3 (0.25mole) of 36% hydrochloric acid was refluxed for 12hrs. After cooling the reaction mixture was poured into 100cm^3 of water and neutralized with an aqueous ammonia. The precipitate was filtered off and boiled with 100cm^3 of 4% NaOH. The insoluble product was filtered, washed with water and crystallized from ethanol-water mixture. M.p. 158–160 °C, 0.9g (82.5% yield).

Analyssis:
For $C_{10}H_{10}N_4S$ (218.278) Calcd.: 25.7% N
Found: 24.9% N

Method V

10mmole of N^3-phenyl-2-picolineamidrazone dihydrochloride and 10mmole of allylisothiocyanate in 20cm^3 of anhydrous ethanol was refluxed for 20 hrs. The solvent was distilled off. The residue was boiled with 100cm^3 of 4% NaOH. The precipitate was filtered off, washed with water and crystallized from ethanol-water mixture. M.p. 135–136 °C, 0.8g (36.7% yield).

Analysis: :
For $C_{10}H_{10}N_4S$ (218.278) Calcd.: 25.7% N
Found: 25.3% N

Method VI

10mmole of N^3-phenyl-2-picolineamidrazone dihydrochloride and 10mmole of allylisothiocyanate in 25cm^3 of N,N-dimethylformamide was refluxed for 5 hrs. The solvent was distilled off. The residue was washed several times with water. The crude product was crystallized from ethanol-water mixture. M.p. 153–155 °C, 0.7g (32.1% yield).

For $C_{10}H_{10}N_4S$ (218.278) Calcd.: 25.7% N
Found: 25.4% N

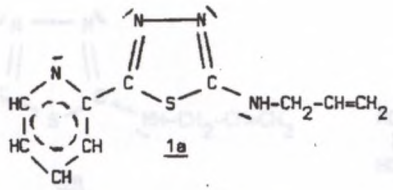
REFERENCES

[1] K o r n i s G., *Comprehensive Heterocyclic Compounds*, vol. 6, 545–577, ed. A.R. Katritzky, W.C. Rees, Pergamon Press, London 1984.
[2] S t r z e m e c k a L., *Polish J. Chem.*, 64, 157, (1990).
[3] B a r n i k o w G., A b r a h a m W., *Z. Chem.*, 5, 183, (1969).

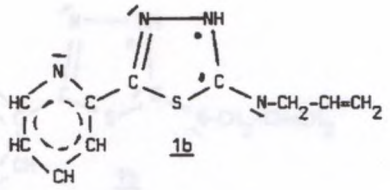
STRESZCZENIE

Na podstawie widm ^{1}H NMR 5-(2'-pirydylo-)2-allilo-(cynamylo-)amino 1,3,4-tiadiazolu stwierdzono obecność tautomerycznych struktur abc oraz ich polarnych form. Przesunięcia chemiczne protonów grupy –N–CH_2– podstawników allilowego i cynamylowego wskazują na różnice w hybrydyzacji orbitali atomowych egzocyklicznego atomu azotu. Otrzymano 5-(2'-pirydylo-)2-alliloamino-1,3,4-tiadiazol.

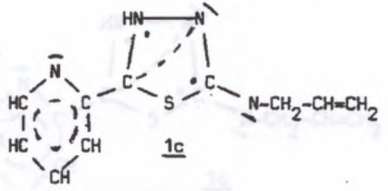
Table 1. Spectral data



1a



1b



1c

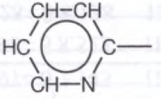
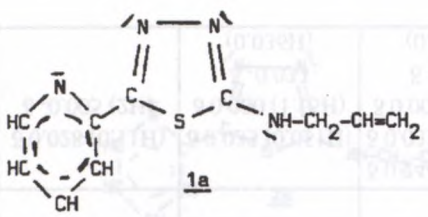
Spectrum No	$CH_2=$	$-CH=$	$-N-CH_2-$	
1	2	3	4	5
I	δ 5.458– δ 5.196 2H	δ 6.101– δ 5.778 1H	δ 4.079– δ 3.999 2H	δ 8.594– δ 8.519 1Hα δ 8.232– δ 8.143 1Hγ δ 7.847– δ 7.674 1Hβ δ 7.336– δ 7.200 1Hβ
II	δ 5.463– δ 5.196 2H	δ 6.106– δ 5.782 1H	δ 4.083– δ 4.003 2H	δ 8.580– δ 8.537 1Hα δ 8.237– δ 8.148 1Hγ δ 7.847– δ 7.674 1Hβ δ 7.336– δ 7.200 1Hβ
III	δ 5.477– δ 5.182 2H	δ 6.111– δ 5.787 1H	δ 4.088– δ 4.003 2H	δ 8.598– δ 8.537 1Hα δ 8.237– δ 8.148 1Hγ δ 7.847– δ 7.674 1Hβ δ 7.331– δ 7.195 1Hβ

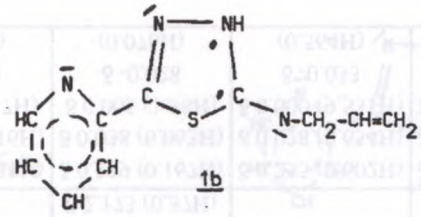
Table 1. – continued

1	2	3	4	5
IV	δ 5.482– δ 5.186 2H	δ 6.111– δ 5.787 1H	δ 4.088– δ 4.003 2H	δ 8.603– δ 8.528 1Hα δ 8.242– δ 8.152 1Hγ δ 7.852– δ 7.683 1Hβ δ 7.341– δ 7.204 1Hβ
V	δ 5.468– δ 5.177 2H	δ 6.101– δ 5.778 1H	δ 4.088– δ 4.008 2H	δ 8.589– δ 8.514 1Hα δ 8.387– δ 8.345 1Hα δ 8.223– δ 8.143 1Hγ δ 8.077– δ 7.974 1Hγ δ 7.838– δ 7.646 1Hβ δ 7.397– δ 7.143 1Hβ
VI	δ 5.482– δ 5.196 2H	δ 6.106– δ 5.782 1H	δ 4.083– δ 4.003 2H	δ 8.598– δ 8.523 1Hα δ 8.228– δ 8.138 1Hγ δ 7.852– δ 7.678 1Hβ δ 7.336– δ 7.200 1Hβ

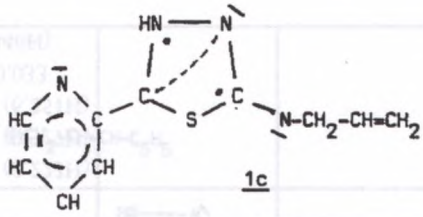
Table 2. Spectral data



1a



1b



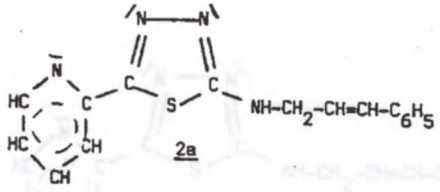
1c

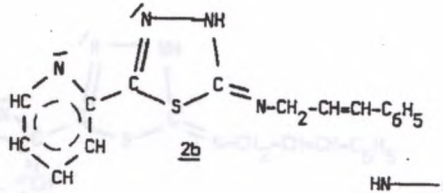
NH							
Spectrum No							
1	2	3	4	5	6	7	8
I	II	III	IV	V	VI	VI_3	VI_4
δ 8.594 – δ 8.519	δ 8.580 – δ 8.537	δ 8.598 – δ 8.537	—	δ 8.589 – δ 8.514	δ 8.598 – δ 8.523		
0.38H	0.08H	0.23H		0.637H	0.1H		
δ 8.232 – δ 8.143	δ 8.237 – δ 8.148	δ 8.237 – δ 8.148	δ 8.242 – δ 8.152	δ 8.387 – δ 8.345	δ 8.228 – δ 8.138		
0.38H	0.1H	0.18H	0.07H	0.705H	0.172H		
δ 7.847 – δ 7.674	δ 7.847 – δ 7.674	δ 7.847 – δ 7.674	δ 7.852 – δ 7.683	δ 8.223 – δ 8.143	δ 7.852 – δ 7.678		
0.43H	0.18H	0.25H	0.13H	0.633H	0.14H		
δ 7.336 – δ 7.200	δ 7.336 – δ 7.200	δ 7.331 – δ 7.195	δ 7.341 – δ 7.204	δ 8.077 – δ 7.974	δ 7.336 – δ 7.200	δ 7.317 (0.74H)	
0.9H	0.43H	0.41H	0.46H	0.756H	0.522H	δ 7.256 (0.34H)	
				δ 7.838 – δ 7.646		δ 7.233 (2H)	δ 7.233 (2H)
				1.356H		δ 7.125 (2.09H)	δ 7.120 (3.03H)
				δ 7.397 – δ 7.143		δ 7.040 (0.786H)	δ 7.035 (0.802H)
				5.222H			

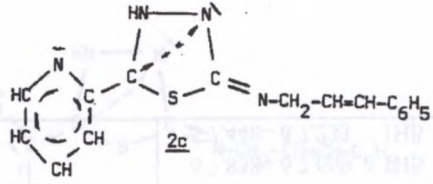
Table 2. – continued

1	2	3	4	5	6	7	8
δ 6.657 (1H) δ 6.101 – δ 5.778 0.53H	δ 6.674 (1H) δ 6.162 (0.045H) δ 6.106 – δ 5.782 0.071H	δ 6.683 (1H) δ 6.167 (0.37H) δ 6.111 – δ 5.787 0.019H	δ 6.500 (1.009H) δ 6.111 – δ 5.787 0.03H	δ 6.683 (1.142H)	δ 6.632 (1H) δ 6.106 – δ 5.782 0.03H		
δ 5.458 – δ 5.196 0.738H	δ 5.463 – δ 5.196 0.3H	δ 5.477 – δ 5.182 0.26H	δ 5.482 – δ 5.186 0.24H	δ 5.468 – δ 5.177 0.9H	δ 5.482 – δ 5.196 0.338H		
δ 4.079 – δ 3.999 0.822H	δ 4.083 – δ 4.003 0.4H	δ 4.088 – δ 4.003 0.2H	δ 4.088 – δ 4.003 0.37H	δ 4.088 – δ 4.008 1.359H	δ 4.083 – δ 4.003 0.662H	δ 4.018 (0.19H) δ 3.999 (0.183H) δ 3.910 (0.326H) δ 3.981 (0.318H) δ 3.623 (0.07H) δ 3.581 (0.137H) δ 3.562 (0.143H) δ 3.412 (0.480H) δ 3.304 (0.466H) δ 3.206 (0.09H)	δ 4.018 (0.192H) δ 3.999 (0.200H) δ 3.905 (0.886H) δ 3.407 (0.759H) δ 3.299 (0.671H)
			δ 2.173 (0.37H)				
δ 0.028 (0.11H) δ -0.005 (2H)	δ 0.033 (0.051H) δ 0.000 (1.15H) δ -0.033 (0.036H)	δ 0.244 (0.131H) δ 0.033 (0.116H) δ 0.000 (2.17H) δ -0.033 (0.099H)	δ 0.239 (0.167H) δ 0.038 (0.063H) δ 0.005 (1.38H) δ -0.028 (0.076H)	δ 0.235 (0.602H) δ 0.028 (0.654H) δ 0.000 (9.531H) δ -0.033 (0.564H)	δ 0.244 (0.223H) δ 0.033 (0.327H) δ 0.000 (6.251H) δ -0.033 (0.446H)		

Table 3. Spectral data







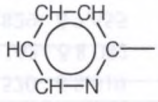
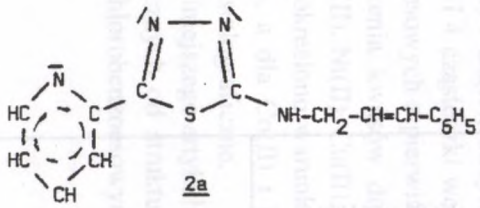
Spectrum No	—N—CH_2—	—CH=CH—	—C_6H_5	
1	2	3	4	5
VII	δ 4.266– δ 4.210 2H	δ 6.660 1H δ 6.430– δ 6.153 1H	δ 7.444– δ 7.242 5H	δ 8.580– δ 8.533 1Hα δ 8.176– δ 8.096 1Hγ δ 7.890– δ 7.674 1Hβ δ 7.444– δ 7.242 1Hβ
VIII	δ 4.224– δ 4.163 2H	δ 6.622 1H δ 6.416– δ 6.144 1H	δ 7.430– δ 7.190 5H	δ 8.547– δ 8.500 1Hα δ 8.143– δ 8.063 1Hγ δ 7.796– δ 7.627 1Hβ δ 7.430– δ 7.190 1Hβ

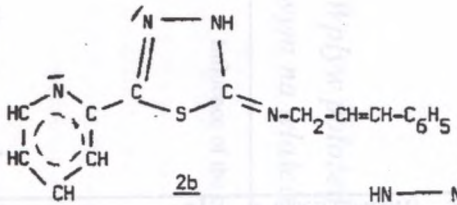
Table 3. – continued

1	2	3	4	5
$VIII_5$	δ 4.2 2H	δ 6.72– δ 6.12 2H	δ7.280 5H	δ 8.48 1Hα δ 8.08 1Hγ δ 7.64 1Hβ δ 7.28 1Hβ
IX	δ 4.252– δ 4.182 2H	δ 6.641– δ 6.144 2H	δ 7.448– δ 7.209 5H	δ 8.570– δ 8.519 1Hα δ 8.162– δ 8.082 1Hγ δ 7.829– δ 7.655 1Hβ δ 7.448– δ 7.209 1Hβ
X	δ 4.257– δ 4.196 2H	δ 6.646– δ 6.134 2H	δ 7.448– δ 7.233 2H	δ 8.570– δ 8.523 1Hα δ 8.162– δ 8.082 1Hγ δ 7.838– δ 7.669 1Hβ δ 7.448– δ 7.233 1Hβ

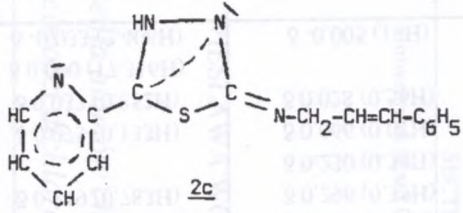
Table 4. Spectral data



2a



2b



2c

NH				
Spectrum No				
1	2	3	4	5
VII	VIII	$VIII_5$	IX	X
	δ 8.547 – δ 8.500	δ 13.64 (s)	δ 8.570 – δ 8.519	δ 8.570 – δ 8.523
	0.61H	δ 8.48 (0.25H)	0.146H	0.03H
δ 8.176 – δ 8.096	δ 8.143 – δ 8.063	δ 8.08 (0.5H)	δ 8.162 – δ 8.082	δ 8.162 – δ 8.082
0.04H	0.742H	δ 7.64 (2.5H)	0.509H	0.273H
δ 7.890 – δ 7.674	δ 7.796 – δ 7.627	δ 7.28 (2.0H)	δ 7.829 – δ 7.655	δ 7.838 – δ 7.669
2H	3.425H		2H	2H
δ 7.444 – δ 7.242	δ 7.430 – δ 7.190		δ 7.448 – δ 7.209	δ 7.448 – δ 7.233
2H	3.08H		1.197H	1.22H

Table 4. – continued

1	2	3	4	5
δ 6.815 (0.48H) δ 6.660 (0.12H) δ 6.430 – δ 6.153 0.83H	δ 6.782 (0.402H) δ 6.416 – δ 6.144 0.31H	δ 6.72 – δ 6.12 0.75H	δ 6.801 (0.353H)	δ 6.805 (0.31H)
δ 4.266 – δ 4.210 0.7H	δ 4.224 – δ 4.163 0.73H	δ 4.2 (0.5H)	δ 4.252 – δ 4.182 0.430H	δ 4.257 – δ 4.196 0.134H
	δ 2.145 (0.016)H			
δ 0.601 (0.183H) δ 0.507 (0.125H) δ 0.253 (0.344H) δ 0.239 (0.171H) δ 0.042 (0.52H)	 δ 0.488 (0.034H) δ 0.225 (0.27H) δ 0.066 (0.115H) δ 0.019 (0.283H)	δ 0.6 (s) δ 0.5 (s) δ 0.24 (s) δ 0.08 (s) δ 0.04 (s)	δ 0.587 (0.162H) δ 0.498 (0.105H) δ 0.249 (0.783H) δ 0.075 (0.133H) δ 0.033 (0.852H) δ 0.000 (17.316H) δ -0.033 (2.406H)	δ 0.587 (0.13H) δ 0.498 (0.17H) δ 0.296 (0.35H) δ 0.230 (0.34H) δ 0.066 (0.07H) δ 0.028 (0.56H) δ -0.005 (13H)