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Tautomerism of 1,3,4–thiadiazole. Part III

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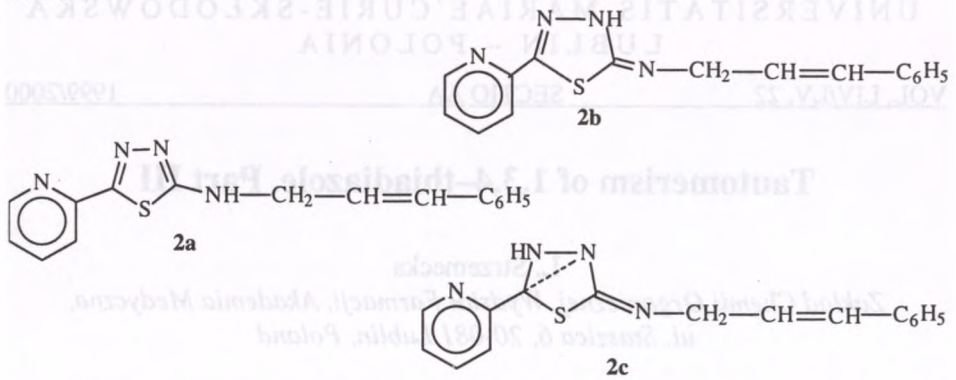
The ^{1}H NMR spectra of 5 -(2'- pyridyl-) 2-cinnamylamino-1,3,4-thiadiazole indicate the presence of the tautomeric modifications **2a 2b 2c**. The chemical shifts values of the protons of cinnamyl substituent indicate the sp^2, sp hybridization of exocyclic nitrogen atom 2N(5N) and the presence of the tautomeric modifications **2a 2b 2c** in both kinds of hybridization. The coupling constants of the protons of cinnamyl substituent support the presence of the structures **$2a_{f'g'}$,$2b_{f'g'}$,$2c_{f'g'}$, $2a_{f'g''}$$2b_{f'g''}$$2c_{f'g''}$, $2a_{fg}$ $2b_{fg}$$2c_{fg}$** as well as the transformation of the structures **$2a_{g''}$$2b_{g''}$$2c_{g''}$** $\rightarrow$ **$2a_{f'}$,$2b_{f'}$,$2c_{f'}$, $2a_{g'}$,$2b_{g'}$,$2c_{g'}$** $\Leftrightarrow$ **$2a_{f'}2b_{f'}2c_{f'}$, $2a_f2b_f2c_f$** $\Leftrightarrow$ **$2a_g2b_g2c_g$**.. The long – range coupling constants confirm the existence of the rigid structures **$2a_{g'''}$$2b_{g'''}$$2c_{g'''}$** and sp hybridization of exocyclic nitrogen atom 2N(5N).

1. INTRODUCTION

Continuing the investigations on the structure of 5-substituted-2-R-amino-1,3,4-thiadiazole [1,2] the ^{1}H NMR spectra of 5-(2'-pyridyl-)2-cinnamylamino-1,3,4-thiadiazole have been examined. In the previous paper [1] it has been stated that the exocyclic nitrogen atom 2N(5N) of 5-(2'-pyridyl-)2-cinnamylamino-1,3,4-thiadiazole **2a** and its tautomeric forms 3H-5-(2'-pyridyl-)2-cinnamylimino-1,3,4-thiadiazole **2b,** 3H-2-(2'-pyridyl-)5-cinnamylimino -1,3,4-thiadiazole **2c** (Scheme 1) may show sp^2, sp hybridization and these tautomers may appear in both kinds of hybridization, the structures **$2a_{fg}$ $2b_{fg}$ $2c_{fg}$,** respectively as well as they may exist as the mesoionic forms **2h 2i 2j,** respectively. The chemistry of some mesoionic forms of 1,3,4-thiadiazole has been described by C.G. Newton and C.A. Ramsden [3,4].

Scheme 1



The purpose of the present paper has been to prove the presence of the tautomeric forms **2a 2b 2c** in both kinds of hybridization on the basis of the ^{1}H NMR spectra (Scheme 1). It has been earlier reported [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 ^{1}H NMR spectra of product **2a 2b 2c** obtained by the cyclization of N^1-(cinnamyl- thiocarbamyl-) N^3-phenyl – 2-picolineamidrazone with diluted or concentrated hydrochloric acid at room or boiling temperature, methods VII, VIII [5]

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 in different solvents, methods IX, X [5]:

IX. boiling anhydrous ethanol

X. boiling N,N-dimethylformamide

have been taken in $CDCl_3$ solution, spectra VII – X, $VIII_5$ [1], $VIII_{8,9}$ and in DMSO solution, spectra $VIII_{6,7,10}$.

The ^{1}H NMR spectra $VIII_{6\text{-}9}$ have been recorded, applaying various concentration of product **2abc** obtained by method VIII in a DMSO or $CDCl_3$ solution:

- in a DMSO solution, the concentration of product **2abc** amounts to (1:3) spectra $VIII_6$, $VIII_7$, respectively
- in $CDCl_3$ solution, the concentration of product **2abc** amounts to: 9 mg/0,5 ccm spectrum $VIII_8$, 18 mg/ 0.5 ccm spectrum $VIII_9$

The ^{1}H NMR spectra VII – X, $VIII_5$ [1] have been recorded in a $CDCl_3$ solution, $VIII_{10}$ in a DMSO solution without any determination of the concentration of **2abc** product.

2. RESULTS AND DISCUSSION

In the ^{1}H NMR spectrum of product **2abc** obtained by method VIII, spectrum $VIII_5$, (Table 1), there appear the signal at δ 13.64 corresponding to the proton of -NH- group of **2c** tautomer. The considerable deshielding of NH proton of **2c** tautomer is caused by intramolecular hydrogen bond.
In the ^{1}H NMR spectra $VIII_{6,7}$ of products **2abc** in a DMSO solution the signal of NH group appears at δ 8.358 (1.5H broaded triplet), δ 8.390 (1.08H degenerated broaded triplet), respectively (Table 1) and analogously to those of **1abc** [2] confirms the presence of **2a 2b 2c** tautomers. These signals disappear in D_2O (Spectrum $VIII_{10}$).

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

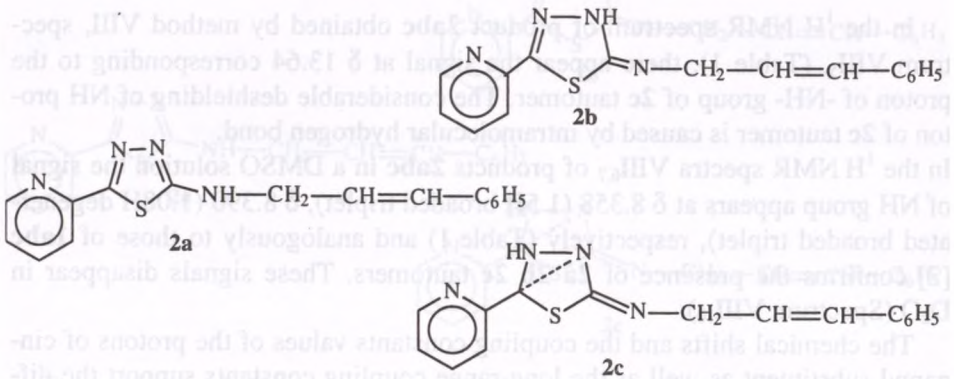
The long-range coupling constants of the protons in the range 37.376 Hz – 43.520 Hz spectra VII – X [1] (Table 2), support the presence of the coupling of the protons of the pyridyl and -N-CH_2-CH=CH-C_6H_5 groups via 2p orbitals of 3'C 3"C of the rigid structures **2a$_{g'''}$ 2b$_{g'''}$ 2c$_{g'''}$** (Scheme 2) and indicate sp hybridization of exocyclic nitrogen atom 2N(5N).

In the ^{1}H NMR spectra $VIII_{6,7}$ triplets at δ 4.115 – 4.218, δ 4.147 – 4.242, respectively, correspond to the protons of -N-CH_2- group of **2a$_{f',g''}$ 2b$_{f',g''}$ 2c$_{f',g''}$** tautomers, (Scheme 3, Table 3) in which the exocyclic nitrogen atom 2N(5N) shows sp^2, sp hybridization, respectively.

In the ^{1}H NMR spectra $VIII_{6,7,10}$ H_b proton of -N-CH_2-CH=CH-C_6H_5 group occurs in form of two triplets: δ 6.461 – 6.480, δ 6.302 – 6.319 that support E and Z isomers, respectively of **2a$_{f',g''}$ 2b$_{f',g''}$ 2c$_{f',g''}$** tautomers. A signal of H_a proton of E isomers of **2a$_{f',g''}$ 2b$_{f',g''}$ 2c$_{f',g''}$** tautomers appears at δ 6.609 – 6.788. The signal of $H_{a'}$ proton of Z isomers of **2a$_{f',g''}$ 2b$_{f',g''}$ 2c$_{f',g''}$** tautomers appears at δ 6.248 – 6.531 (Table 4).

The coupling constants of the protons $J(H_aH_b)$ 16.2Hz, $J(H_bH_a)$ 16.2Hz ($VIII_6$) and $J(H_bH_c)$ 7.9Hz, $J(H_bH_d)$ 6.8Hz, $J(H_bH_{a'})$ 12.1Hz, $J(H_{a'}H_b)$ 12.1Hz ($VIII_{7,10}$) confirm the presence of the structures **2a$_{g''}$ 2b$_{g''}$ 2c$_{g''}$** (Table 4).

Table 1



NH				
Spectrum No				
$VIII_5$ ($CDCl_3$)	$VIII_6$ (DMSO)	$VIII_7$ (DMSO)	$VIII_8$ ($CDCl_3$)	$VIII_9$ ($CDCl_3$)
δ 13.64 (s)	δ 8.635 - 8.560	δ 8.650 - 8.574	δ 8.591 - 8.513	δ 8.574 - 8.499
δ 8.48 (0.25 H)	0.4 H	0.08 H	------	-----
δ 8.08 (0.5 H)	δ 8.411 - 8.306	δ 8.435 - 8.345	----------	----------
δ 7.64 (2.5 H)	1.5 H (t)	1.08 H		
δ 7.28 (2 H)	δ 8.142 - 8.037	δ 8.169 - 8.067	δ 8.213 - 8.110	δ 8.179 - 8.076
	------	-----	-----	-----
	δ 8.003 - 7.835	δ 8.010 - 7.842	δ 7.830 - 7.659	δ 7.798 - 7.627
	0.6 H	-----	0.15 H	-----
	δ 7.522 - 7.224	δ 7.530 - 7.232	δ 7.527 - 7.193	δ 7.447 - 7.129
	2.5 H	0.4 H	0.7 H	0.5 H
δ 6.72 - 6.12	δ 6.771 - 6.248	δ 6.788 - 6.265	δ 6.805 - 6.168	δ 6.785 - 6.165
0.75 H	1.4 H	-----	1.2 H	0.08 H
δ 4.2 (0.5H)	δ 4.218 - 4.115	δ 4.242 - 4.147	δ 4.232 - 4.161	δ 4.215 - 4.147
	0.5 H	0.4 H	0.15 H	-------

Table 2

δ,	J,	(Spectrum No)
δ 6.641	$J(H_{a'}H_{4'})$ 37.376 Hz	(IX)
δ 8.082	$J(H_{4'}H_a)$ 37.632 Hz	(IX)
δ 0.498	$J(H_{NH}H_{6'})$ 38.400 Hz	(X)
	$J(H_{NH}Ha')$	
δ 7.190	$J(H_{3'}H_a)$ 38.784 Hz	(VIII)
δ 4.266	$J(H_dH_{4'})$ 41.472 Hz	(VII)
δ 8.063	$J(H_{4'}H_a)$ 42.496 Hz	(VIII)
δ 7.369	$J(H_{3'}H_a)$ 42.624 Hz	(VIII)
δ 4.210	$J(H_cH_{3'})$ 43.008 Hz	(VII)
δ 7.242	$J(H_{3'}H_a)$ 43.520 Hz	(VII)

The coupling constants of the protons $J(H_bH_c)$ 6.6 Hz, $J(H_bH_d)$ 5.4Hz, $J(H_bH_{a'})$ 12.0 Hz, $J(H_{a'}H_b)$ 12.0 Hz ($VIII_6$) and $J(H_aH_b)$ 16.1Hz, $J(H_bH_a)$ 16.1Hz, $J(H_bH_c)$ 6.6 Hz, $J(H_bH_d)$ 5.4 Hz ($VIII_{7,10}$, Table 4) indicate the transformation of the structures **2a**$_{g''}$ **2b**$_{g''}$ **2c**$_{g''}$ → **2a**$_{f''}$ **2b**$_{f''}$ **2c**$_{f''}$. The different coupling constants of the protons $J(H_bH_d)$ 5.4 Hz, $J(H_bH_c)$ 6.6 Hz, $J(H_bH_d)$ 6.8Hz, $J(H_bH_c)$ 7.9Hz support the existence of the rigid structures **2a**$_{f''}$ **2b**$_{f''}$ **2c**$_{f''}$, **2a**$_{g''}$ **2b**$_{g''}$ **2c**$_{g''}$ (Scheme 3). The transformation of **2a**$_{g''}$ **2b**$_{g''}$ **2c**$_{g''}$ → **2a**$_{f''}$ **2b**$_{f''}$ **2c**$_{f''}$ result from the changes of sp hybridization of 2N(5N) to sp^2 one as well as of sp^2 hybridization of 3"C to sp^3 one.

In the ^{1}H NMR spectra $VIII_{8,9}$ a signal of the protons of -N-CH_2- group arises at δ 4.161 – 4.232 and δ 4.147 – 4.215 as pairs of doublets: δ 4.161 – 4.174, δ 4.220 – 4.232 and δ 4.147 – 4.157, δ 4.203 – 4.215, respectively (Table 3) and support the presence of non-eqivalent protons of AB system of -N-CH_2- group of a rigid structures **2a**$_g$ **2b**$_g$ **2c**$_g$ (Scheme 4).

In the ^{1}H NMR spectrum $VIII_8$ there are present double signals of H_a proton: doublets at δ 6.805 – 6.646 $J(H_aH_b)$ 15.9 Hz, δ 6.792 – 6.634 $J(H_aH_b)$ 15.8 Hz correspond to H_a proton of *E* isomers of **2a**$_g$ **2b**$_g$ **2c**$_g$, **2a**$_f$ **2b**$_f$ **2c**$_f$ tautomers, respectively (Table 4) with sp, sp^2 hybridization of exocyclic nitrogen atom 2N(5N). The triplets at δ 6.417 $J(H_bH_c)$ 9.5 Hz, δ 6.385 $J(H_bH_c)$ 5.9 Hz correspond to H_b proton of *E* isomers of **2a**$_g$ **2b**$_g$ **2c**$_g$, **2a**$_f$ **2b**$_f$ **2c**$_f$ tautomers, respectively. A triplet at δ 6.226 $J(H_bH_d)$ 5.7 Hz, $J(H_bH_d)$ 9.2 Hz corresponds to H_b

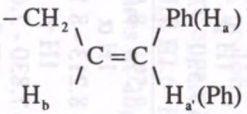
proton of *Z* isomers of **2a$_{fg}$ 2b$_{fg}$ 2c$_{fg}$** tautomers, respectively. The signals of $H_{a'}$ proton of *Z* isomers of **2a$_{fg}$ 2b$_{fg}$ 2c$_{fg}$** tautomers with the coupling constants $J(H_{a'}H_b)$ 12.6 Hz, $J(H_{a'}H_b)$ 13.1 Hz, respectively appears at δ 6.441- 6.168 (Table 4). The coupling constants of the protons $J(H_aH_b)$ 15.9 Hz, $J(H_bH_a)$ 15.9 Hz, $J(H_{a'}H_b)$ 13.1 Hz, $J(H_bH_{a'})$ 13.1 Hz, $J(H_bH_c)$ 9.5 Hz, $J(H_bH_d)$ 9.2 Hz confirm the existence of the rigid structures of **2a$_g$ 2b$_g$ 2c$_g$** tautomers (Scheme 4) with sp hybridization of exocyclic nitrogen atom 2N(5N).

The coupling constants of the protons $J(H_aH_b)$ 15.8 Hz, $J(H_bH_a)$ 15.8 Hz, $J(H_{a'}H_b)$ 12.6 Hz, $J(H_bH_{a'})$ 12.6 Hz, $J(H_bH_c)$ 5.9 Hz, $J(H_bH_d)$ 5.7 Hz indicate the transformation of the rigid structures of **2a$_f$ 2b$_f$ 2c$_f$** ⇔ **2a$_g$ 2b$_g$ 2c$_g$** tautomers, and the changes of δ ⇔ π bonds (Scheme 4). The coupling constants $J(H_bH_c)$ 5.8 Hz, $J(H_bH_d)$ 5.8 Hz, $J(H_{a'}H_b)$ 5.5 Hz, $J(H_bH_{a'})$ 5.5 Hz, point to the lack of the rigid structures and suggest the transformation of **2a$_{f'}$ 2b$_{f'}$ 2c$_{f'}$ 2a$_{g'}$ 2b$_{g'}$ 2c$_{g'}$** structures (Scheme 5) In the ^{1}H NMR spectrum VIII$_9$ the signals at δ 6.785 – 6.627, $J(H_aH_b)$ 15.8 Hz, δ 6.382 $J(H_bH_a)$ 15.8 Hz, $J(H_bH_c)$ 5.9 Hz correspond to H_a, H_b protons, respectively of *E* isomers. The signals of H_b, $H_{a'}$ protons of *Z* isomers appear at δ 6.224 $J(H_bH_d)$ 5.7 Hz, $J(H_bH_{a'})$ 12.6 Hz, δ 6.439 – 6.165 $J(H_{a'}H_b)$ 12.6 Hz, respectively and indicate the transformation of the rigid structures of **2a$_f$ 2b$_f$ 2c$_f$** ⇔ **2a$_g$ 2b$_g$ 2c$_g$** tautomers.

Table 3

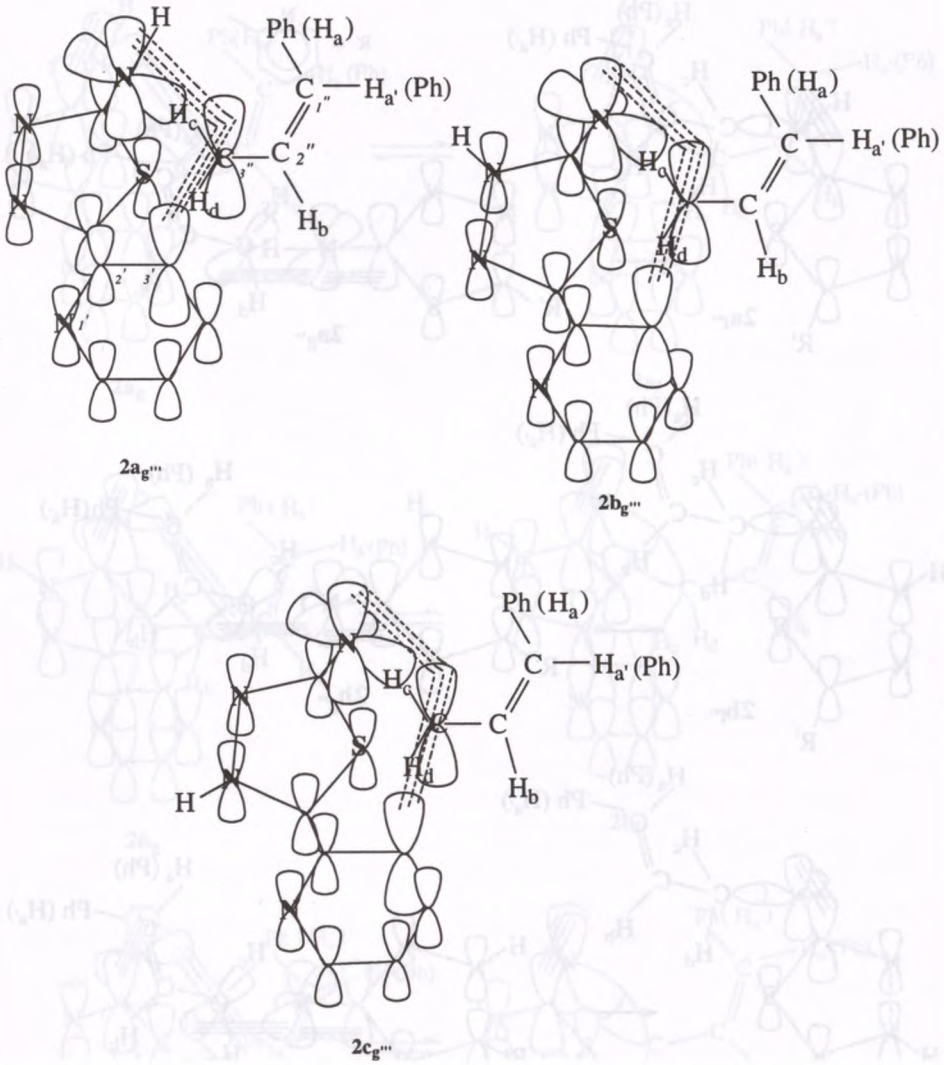
Spectrum No (solvent)	-N-CH_2 -	-CH = CH-	-C_6H_5	2'-pyridyl
$VIII_6$ (DMSO)	δ 4.218 - 4.115 2H m	δ 6.771 - 6.248 2H m	δ 7.522 - 7.224 5H m	δ 8.635 - 8.560 1H α δ 8.142 - 8.037 1H γ δ 8.003 - 7.835 1H β δ 7.522 - 7.224 1H β
$VIII_7$ (DMSO)	δ 4.242 - 4.147 2H m	δ 6.788 - 6.265 2H m	δ 7.530 - 7.232 5H m	δ 8.650 - 8.574 1H α δ 8.169 - 8.067 1H γ δ 8.010 - 7.842 1H β δ 7.530 - 7.232 1H β
$VIII_8$ ($CDCl_3$)	δ 4.232 - 4.161 2H m	δ 6.805 - 6.168 2H m	δ 7.527 - 7.193 5H m	δ 8.591 - 8.513 1H α δ 8.213 - 8.110 1H γ δ 7.830 - 7.659 1H β δ 7.527 - 7.193 1H β
$VIII_9$ ($CDCl_3$)	δ 4.215 - 4.147 2H m	δ 6.785 - 6.165 2H m	δ 7.447 - 7.129 5H m	δ 8.574 - 8.499 1H α δ 8.179 - 8.076 1H γ δ 7.798 - 7.627 1H β δ 7.447 - 7.129 1H β
$VIII_{10}$ (DMSO + D_2O)	δ 4.220 - 4.169 2H m	δ 6.785 - 6.251 2.4H m	δ 7.527 - 7.207 5H m	δ 8.650 - 8.577 1H α δ 8.164 - 8.099 1H γ δ 8.032 - 7.864 1H β δ 7.527 - 7.207 1.4H β

Table 4



Spe ctrum No solvent	**2a$_{f'}$ 2b$_{f'}$2c$_{f'}$**				**2a$_{g'}$2b$_{g'}$2c$_{g''}$**			
	trans (E)		*cis (Z)*		*Trans (E)*		*cis (Z)*	
	H$_b$	**H$_a$**	**H$_b$**	**H$_{a'}$**	**H$_b$**	**H$_a$**	**H$_b$**	**H$_{a'}$**
1	2	3	4	5	6	7	8	9
VIII$_6$ DMSO	δ 6,461 J(H$_b$H$_c$) 6,6Hz	-	δ 6,302 J(H$_b$H$_d$) 5,4Hz J(H$_b$H$_{a'}$) 12,0Hz	δ 6,514 – 6,248 J(H$_{a'}$H$_b$) 12,0Hz	δ 6,461 J(H$_b$H$_a$) 16,2Hz	δ 6,771- 6,609 J(H$_a$H$_b$) 16,2Hz	-	-
VIII$_7$ DMSO	δ 6,480 J(H$_b$H$_c$) 6,6Hz J(H$_b$H$_a$) 16,1Hz	δ 6,788 - 6,627 J(H$_a$H$_b$)16,1Hz	δ 6,319 J(H$_b$H$_d$) 5,4Hz	-	δ 6,480 J(H$_b$H$_c$) 7,9Hz	-	δ 6,319 J(H$_b$H$_d$) 6,8Hz J(H$_b$H$_{a'}$) 12,1Hz	δ 6,531 – 6,265 J(H$_{a'}$H$_b$) 12,1Hz
VIII$_{10}$ DMSO + D$_2$O	δ 6,465 J(H$_b$H$_c$) 6,6Hz J(H$_b$H$_a$) 16,1Hz	δ 6,785 – 6,624 J(H$_a$H$_b$) 16,1Hz	δ 6,304 J(H$_b$H$_d$) 5,4Hz	-	δ 6,465 J(H$_b$H$_c$) 7,9Hz	-	δ 6,304 J(H$_b$H$_d$) 6,8Hz J(H$_b$H$_{a'}$) 12,1Hz	δ 6,519 – 6,251 J(H$_{a'}$H$_b$) 12,1Hz
	2a$_f$2b$_f$2c$_f$				**2a$_g$ 2b$_g$ 2c$_g$**			
1	2	3	4	5	6	7	8	9
VIII$_8$ CDCl$_3$	δ 6,385 J(H$_b$H$_c$) 5,9Hz J(H$_b$H$_a$) 15,8Hz	δ 6,792 – 6,634 J(H$_a$H$_b$) 15,8Hz	δ 6,226 J(H$_b$H$_d$) 5,7Hz J(H$_b$H$_{a'}$) 12,6Hz	δ 6,420 – 6,294 J(H$_{a'}$H$_b$)12,6Hz	δ 6,417 J(H$_b$H$_c$) 9,5Hz J(H$_b$H$_a$) 15,9Hz	δ 6,805 – 6,646 J(H$_a$H$_b$) 15,9Hz	δ 6,226 J(H$_b$H$_d$) 9,2Hz J(H$_b$H$_{a'}$) 13,1Hz	δ 6,441 – 6,168 J(H$_{a'}$H$_b$) 13,1Hz
VIII$_9$ CDCl$_3$	δ 6,382 J(H$_b$H$_c$) 5,9Hz J(H$_b$H$_a$) 15,8Hz	δ 6,785 – 6,627 J(H$_a$H$_b$) 15,8Hz	δ 6,224 J(H$_b$H$_d$) 5,7Hz J(H$_b$H$_{a'}$) 12,6Hz	δ 6,439 – 6,165 J(H$_{a'}$H$_b$) 12,6Hz	-	-	-	-
	2a$_{f'}$ 2b$_{f'}$2c$_{f'}$				**2a$_{g'}$ 2b$_{g'}$2c$_{g'}$**			
1	2	3	4	5	6	7	8	9
VIII$_8$ CDCl$_3$	δ 6,385 J(H$_b$H$_c$) 5,8Hz	-	δ 6,226 J(H$_b$H$_d$) 5,8Hz J(H$_b$H$_{a'}$) 5,5Hz	δ 6,441 – 6,168 J(H$_{a'}$H$_b$) 5,5Hz	δ 6,417 J(H$_b$H$_c$) 5,8Hz	-	δ 6,226 J(H$_b$H$_d$) 5,8Hz J(H$_b$H$_{a'}$) 5,5Hz	δ 6,441 – 6,168 J(H$_{a'}$H$_b$) 5,5Hz

Scheme 2


H
Ph (Ha)
C
Ha' (Ph)
Hc
C 2"
S
Hd
Hb
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H
Ph (Ha)
C
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Hc
C
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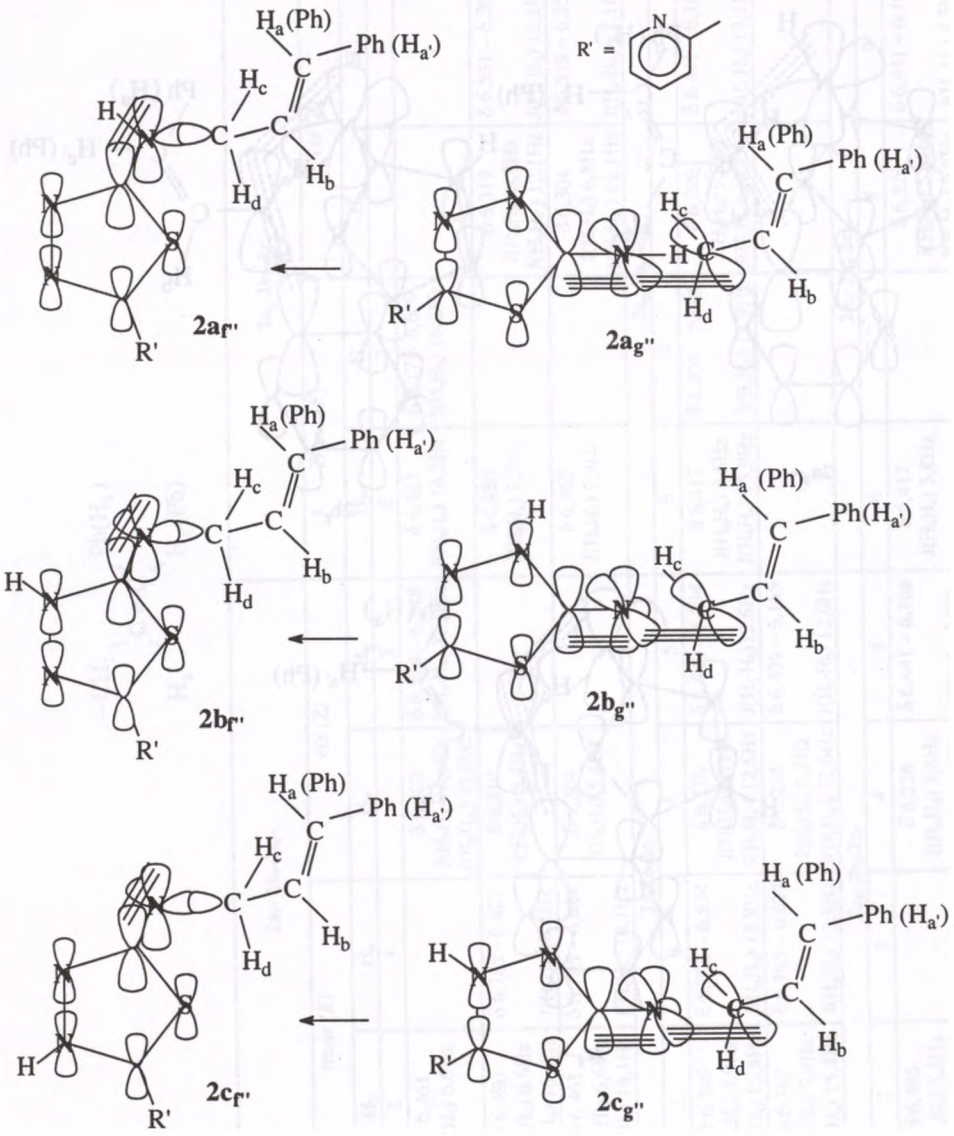
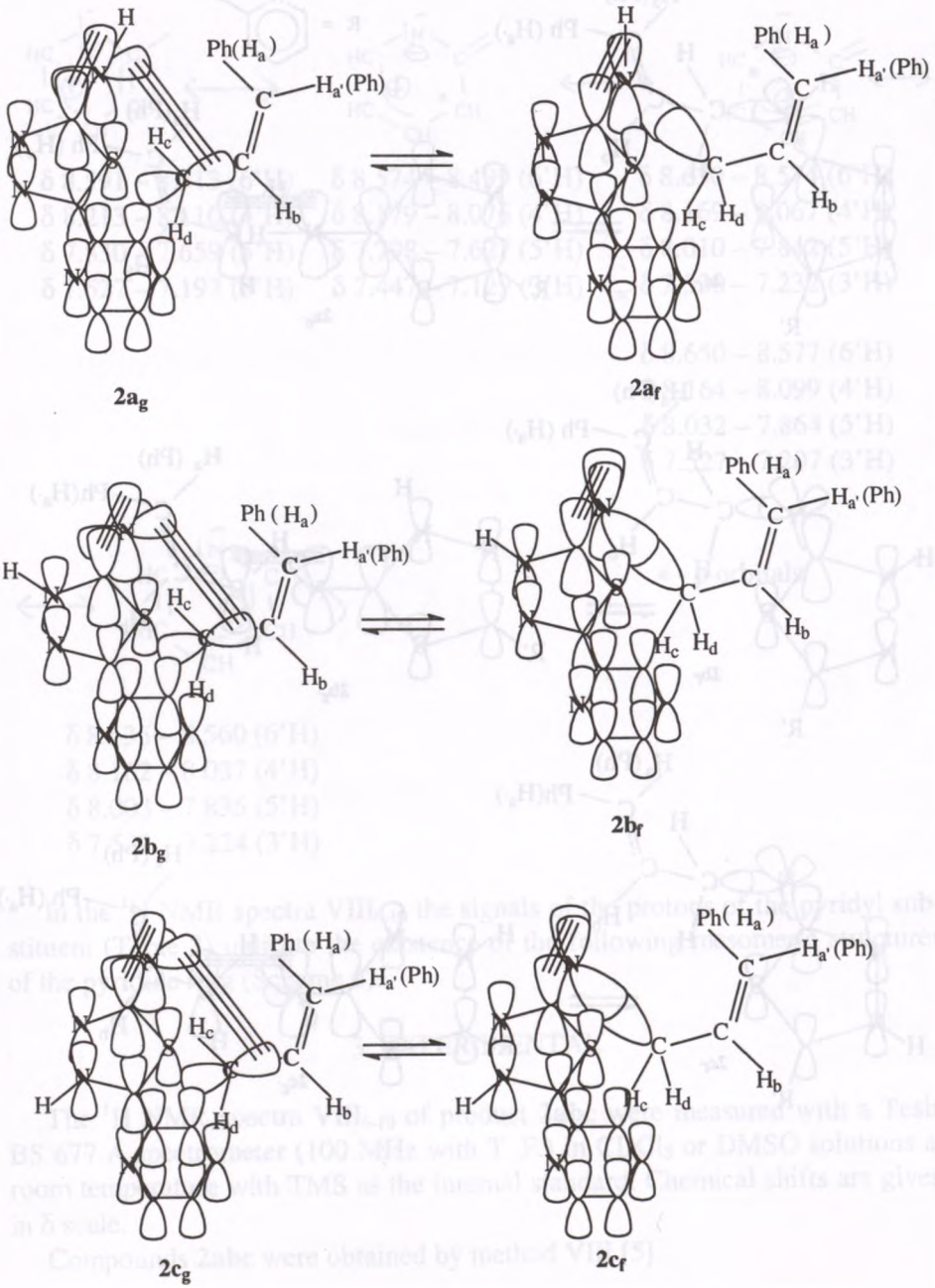
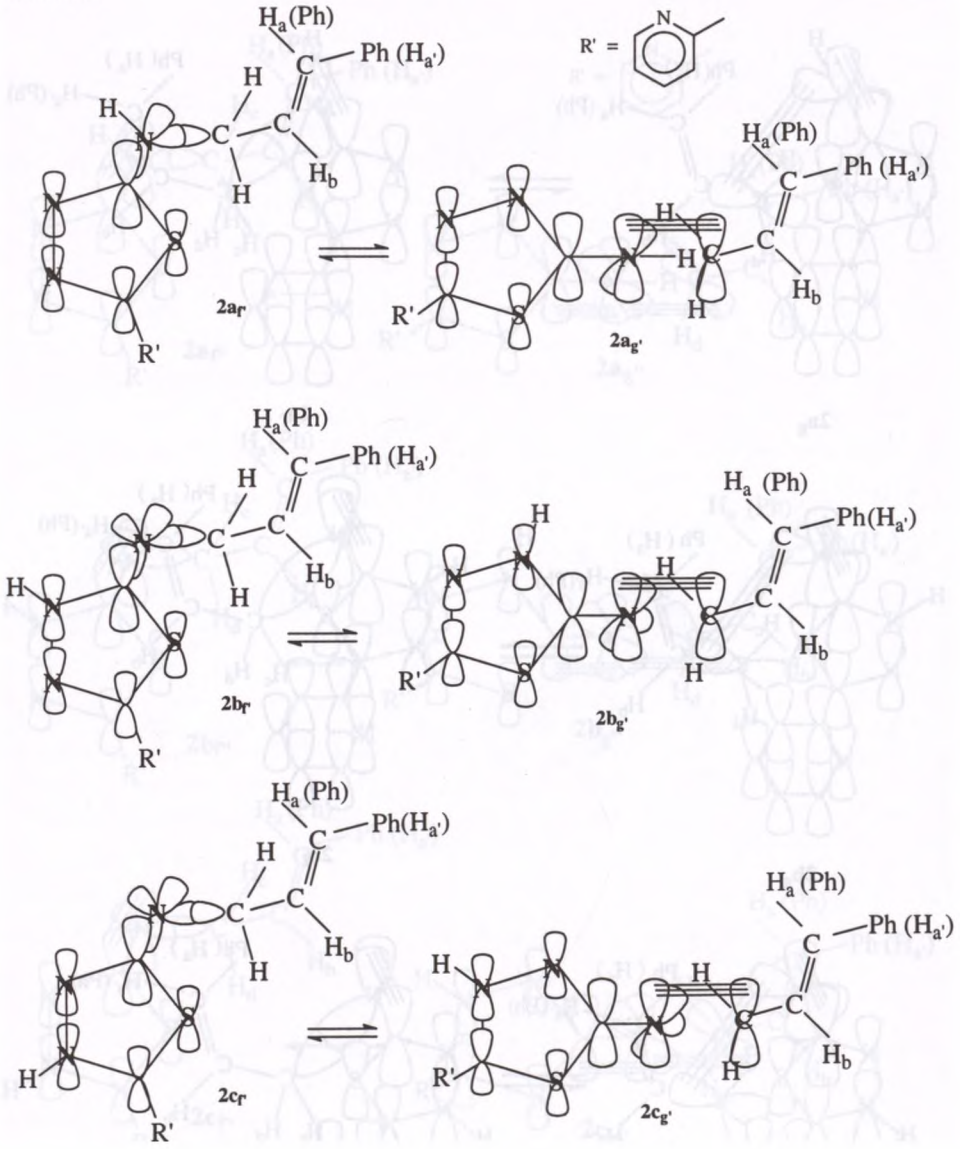
Scheme 3



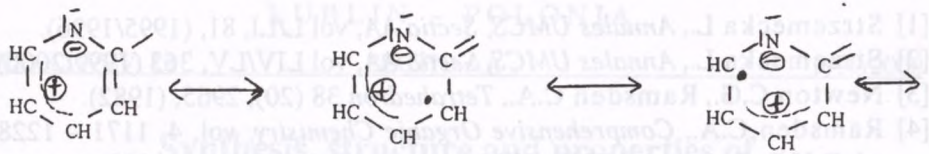
Scheme 4



Scheme 5



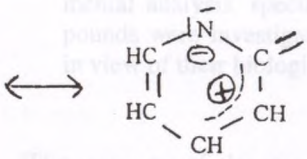
Scheme 6



δ 8.591 – 8.513 (6'H)
δ 8.213 – 8.110 (4'H)
δ 7.830 – 7.659 (5'H)
δ 7.527 – 7.193 (3'H)

δ 8.574 – 8.499 (6'H)
δ 8.179 – 8.076 (4'H)
δ 7.798 – 7.627 (5'H)
δ 7.447 – 7.129 (3'H)

δ 8.650 – 8.574 (6'H)
δ 8.169 – 8.067 (4'H)
δ 8.010 – 7.842 (5'H)
δ 7.530 – 7.232 (3'H)



δ 8.650 – 8.577 (6'H)
δ 8.164 – 8.099 (4'H)
δ 8.032 – 7.864 (5'H)
δ 7.527 – 7.207 (3'H)

• - p orbitals

δ 8.635 – 8.560 (6'H)
δ 8.162 – 8.037 (4'H)
δ 8.003 – 7.835 (5'H)
δ 7.522 – 7.224 (3'H)

In the ^{1}H NMR spectra VIII$_{6\text{-}10}$ 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 ^{1}H NMR spectra VIII$_{6\text{-}10}$ of product **2abc** were measured with 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. Chemical shifts are given in δ scale.

Compounds **2abc** were obtained by method VIII [5]

4. REFERENCES

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