

About the Structure of *N*-Hetaryl Substituted Formamidoximes

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Sir:

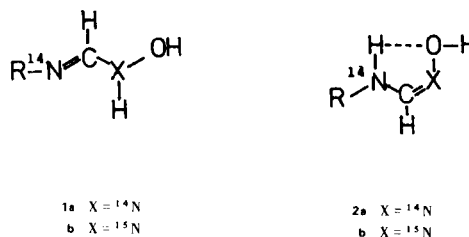
N-Hetaryl-substituted formamidoximes are obtained from the corresponding *N,N*-dimethylaminomethylene-amino compounds and hydroxylamine (1). Since they are important intermediates in the synthesis of *s*-triazoloazines fused at N₂-C₃ bond of the triazole ring (1) it seemed worthwhile to determine their structure.

The nmr spectra of the formamidoxime part of the molecule (Table I) exhibit in d₆-DMSO two doublets for NH-CH group with the coupling constant ³J_{NH-CH} = 10,5 Hz and a singlet for OH group. The comparison of ³J_{NH-CH} with the corresponding coupling constants ³J_{NH-CH} *trans* = 12-14 Hz in *N*-(pyrimidinyl-6)amino-methylenecyanoacetates (2), in enol form of Schiff bases (3) and in *N*-substituted β-aminoacrylic acid derivatives (4) show that both protons are *trans* to each other. On the basis of this information two structures **1a** and **2a** can be drawn.

The simplest method to differentiate between these two structures is the introduction of ¹⁵N (X=¹⁵N) with hydroxylamine 95% enriched in ¹⁵N in the molecule. It has been previously demonstrated that ¹J_{15N-H} coupling constants in different ¹⁵NH containing compounds fall in the range 70-95 Hz (5,6,7), in formamides couplings between ¹⁵N and the formyl proton ²J_{15N-C-H} are found in the range 14-16 Hz (8), while in *N'*-aryl-*N,N*-dimethylformamidines-¹⁵N in the range 7,5-8,4 Hz (9). On the other hand, ²J_{15N=C-H} coupling constants in oximes are dependent on the orientation of the nitrogen lone electron pair. The measured coupling constants are 3 Hz and 16 Hz for *syn* and *anti* isomers, respectively (10,11). Geminal coupling constants between ¹⁵N and proton across a heteroatom are usually not observed because of the facile hydrogen exchange (7). The only reported example is ²J_{15N-O-H} = 2,6 Hz for *O*-protonated conjugate acid of dibenzylnitrosamine-¹⁵N (12).

In our case, the nmr spectra of the corresponding *N*-hetaryl-substituted formamidoximes-¹⁵N (Table I) show a doublet for NH group with ³J_{NH-CH} = 10,5 Hz and a doublet of doublet for CH group with ³J_{NH-CH} = 10,5 Hz and ²J_{15N=C-H} = 16,5-17,2 Hz. On the basis of this information, the structure **1b** is excluded, since there a

large coupling ¹J_{15N-H} in the range 70-95 Hz is not present. The magnitude of the ²J_{15N=C-H} is characteristic for the *cis* orientation of the ¹⁵N lone electron pair with respect to the C-H bond (*i.e.* *anti* form) (10). Furthermore, the doublet for OH group ²J_{15N-O-H} = 1,5-2,0 Hz means that proton of the hydroxy group is oriented *cis* with respect to the ¹⁵N lone pair, most probably because of the intramolecular hydrogen bond formation.



These results are in agreement with the structure **2b** only.

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TABLE I

Nmr Spectra of R-NHCH=XOH (δ values) in d_6 -DMSO, TMS as Internal Standard (a)

R	$X = {}^{14}\text{N}$			$X = {}^{15}\text{N}$						
	NH	CH	OH	JNHCH	NH	CH	OH	JNHCH	$J_{15\text{N}=\text{CH}}$	$J_{15\text{N}-\text{OH}}$
4-Methylpyridyl-2	9,15 (d)	7,80 (d)	10,0 (s)	10,5 Hz	9,10 (d)	7,80 (dd)	10,0 (d)	10,5 Hz	16,5 Hz	1,5 Hz
4,6-Dimorpholino-1,3,5-triazinyl-2	8,14 (d)	7,64 (d)	10,25 (s)	10,5 Hz	8,35 (d)	7,80 (dd)	10,40 (d)	10,5 Hz	16,5 Hz	1,5 Hz
Pyridazinyl-3	9,75 (d)	8,10 (d)	10,45 (s)	10,5 Hz	9,65 (d)	7,96 (dd)	10,40 (d)	10,5 Hz	17,2 Hz	2,0 Hz

(a) Spectra were recorded with an JEOL JNM C-60 HL nmr instrument.

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