

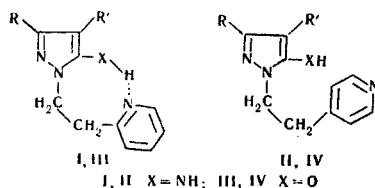
POSSIBILITY OF INTRAMOLECULAR HYDROGEN BONDING
IN 1- $[\beta$ -(2-PYRIDYL)ETHYL]-5-AMINO(OR HYDROXY)PYRAZOLES

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It is shown on the basis of IR spectral and dipole moment data that the formation of a seven-membered cyclic structure is possible in 1- $[\beta$ -(2-pyridyl)ethyl]-5-amino(or hydroxy)-pyrazoles, stabilized by intramolecular hydrogen bonds.

Investigation of the IR spectra and determination of the dipole moments of 1- $[\beta$ -(2-pyridyl)ethyl]-5-aminopyrazoles (I) have shown that these compounds are characterized in the crystalline state by intermolecular association, whereas in solution they form seven-membered rings with intramolecular hydrogen bonds (IHB) between the amino group and the nitrogen of the pyridine ring.



The IR spectra of I (in fluorinated hydrocarbon pastes) in the LiF prism region show absorptions at 3340-3310 ($\nu_{\text{as}}\text{NH}_2$) and 3150-3170 ($\nu_{\text{s}}\text{NH}_2$) cm^{-1} , indicating intermolecular association of the $\text{NH}_2 \dots \text{N} \llcorner$ type. Solution in CCl_4 (c 0.08, 0.04, 0.008 and 0.006 M) results in dissociation which is reflected in a reduction in the intensity of the bands mentioned. At the same time, bands appear at 3430 (ν_{as}) and 3275-3280 (ν_{s}) cm^{-1} , which are characteristic of IHB of the $\text{NH} \dots \text{N}$ type [1]. The formation of IHB is in agreement with the departure of the experimental value for $\nu_{\text{s}}\text{NH}_2$ from that calculated from the formula [2] $\nu_{\text{s calc}} = 345.5 + 0.876 \nu_{\text{as}} = 3350 \text{ cm}^{-1}$. This interpretation is also supported by the experimental values for the dipole moments (see Table 1) which are almost identical with those calculated according to [3] for the structure with IHB (I).

In the case of compounds of type II, which contain the 4-pyridyl residue, intermolecular association occurs in the solid state, the IR spectra having absorptions at 3340-3310 and 3150-3170 cm^{-1} . In CCl_4 , however, the frequency $\nu_{\text{s}}\text{NH}_2$ occurs at 3352 cm^{-1} (ν_{as} 3425 cm^{-1}), which is in satisfactory agreement with that calculated (3344 cm^{-1}) for the free NH_2 group.

The hydroxy analogs, 1- $[\beta$ -(2-pyridyl)ethyl]-5-hydroxypyrazoles (III), are of considerable interest in connection with the above. In the IR spectra of III in the solid phase (KBr disks), stretching vibrations of the C=O group are absent, and strong absorption occurs at 2200-2600 and 3400-3500 cm^{-1} . The former of these frequencies is assigned to stretching of the OH group involved in strong intermolecular association, accompanied by the formation of an immonium structure of the type $\text{>}\ddot{\text{O}} \dots \text{HN}^+ \llcorner$ [4], and the latter to

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TABLE 1. Dipole Moments of 1- $[\beta$ -Pyridyl]ethyl]-5-amino(or hydroxy)-pyrazoles in Dioxane and Benzene*

Compound	X	R	R'	μ_{exp} , 25	$\mu_{\text{calc}}^{\text{IHB}}$
I	NH	$\text{CH}_2\text{C}_6\text{H}_5$	C_6H_5	3.66 (3.13)	3.21
I	NH	C_6H_{11}	C_6H_9	4.03 (3.12)	3.18
I	NH	C_6H_7	C_6H_5	2.97 (2.92)	3.18
I	NH	C_2H_5	CH_3	4.05 (3.32)	3.18
I	NH	$p\text{-H}_2\text{N} \cdot \text{C}_6\text{H}_4$	H	3.01	3.34
II	NH	C_6H_{11}	C_6H_9	(2.82)	
II	NH	$\text{CH}_2\text{C}_6\text{H}_5$	C_6H_5	3.41	
II	NH	$p\text{-H}_2\text{N} \cdot \text{C}_6\text{H}_4$	H	4.09	
III	O	CH_3	H	3.70	3.62
III	O	C_6H_5	CH_3	4.37 (4.17)	3.89
III	O	$p\text{-O}_2\text{N} \cdot \text{C}_6\text{H}_4$	H	6.80	7.70
III	O	$p\text{-H}_3\text{CO} \cdot \text{C}_6\text{H}_4$	H	4.37 (4.07)	3.54
III	O	$p\text{-H}_2\text{N} \cdot \text{C}_6\text{H}_4$	H	5.41	3.20
IV	O	C_6H_5	H	3.45 (3.16)	
IV	O	$p\text{-H}_3\text{CO} \cdot \text{C}_6\text{H}_4$	H	5.77 (4.64)	
IV	O	$p\text{-H}_2\text{N} \cdot \text{C}_6\text{H}_4$	H	6.51	

*The values of μ for solutions in benzene are given in parentheses.

ν_{OH} , participating in the normal intramolecular hydrogen bonding of the $\text{OH} \dots \text{N} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ type, or possibly with the formation of IHB of the III type. Thus, in the crystalline state, compounds III exist exclusively in the hydroxy form. In solution, irrespective of the nature of the solvent, III exist predominantly in the oxo form, strong absorptions being present in the IR spectra due to stretching of the C=O group: 1713 (CCl_4), 1707 (dioxane), and 1696 cm^{-1} (CHCl_3). In addition, in the LiF prism region, weak absorption occurs in solutions at 3390 and 3752 cm^{-1} . The former of these bands disappears on dilution to $2 \cdot 10^{-4}$ M, while the latter persists together with a weak band due to the free OH at 3615 cm^{-1} . The band at 3572 cm^{-1} should apparently be assigned to IHB of type III. This latter conclusion is in agreement with the more complete conversion to the oxo form of IV on solution, in which the formation of IHB is structurally impossible. However, the small reduction in the OH stretching frequency in III (by 40 cm^{-1} in all) and the poorer correspondence of μ_{exp} with μ_{calc} than in the case of I (see Table 1) show that the IHB in the hydroxy derivatives III are not strong and that consequently their energy is insufficient for full stabilization of the hydroxy forms in solution.

EXPERIMENTAL

The synthesis of the 1- $[\beta$ -(pyridyl)ethyl]-5-aminopyrazoles (I-II) was carried out by boiling an equimolecular mixture of the appropriate pyridylethylhydrazines [5] and iminonitriles in tert-butanol in presence of a catalytic amount of glacial acetic acid, for 12 h. The properties of the compounds obtained are given in [6].

1- $[\beta$ -Pyridyl]ethyl]-5-hydroxypyrazoles (III, IV) were obtained according to [7].

IR spectra were taken on an IKS-14A instrument. The dipole moments (see Table 1) were determined in benzene and dioxane at 25°, by the method described previously [8].

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