# INTRAMOLECULAR π-HYDROGEN BONDING IN 5-(β-HYDROXYETHYL)-1,2-DIHYDROPYRROLIZINE

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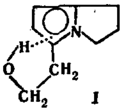
UDC 547.466.46'744:543.422.4

The presence of two absorption bands at 3580 ($\varepsilon^a$ 17) and 3640 cm$^{-1}$ ($\varepsilon^a$ 24) is detected in the region of the stretching vibrations of the hydroxyl group in sufficiently dilute solutions of 5-(β-hydroxyethyl)-1,2-dihydropyrrolizine (I) in $CCl_4$.

A study of the concentration trend of the intensities of these bands showed the concentration independence of their $\varepsilon^a$ values, typical for intramolecular hydrogen bonding [1].

Considering the position and form of the bands as well as their behavior as the concentration of the compound is changed, it can be assumed that the absorption at 3580 cm$^{-1}$ pertains to the vibrations of the hydroxyl group involved in the formation of a hydrogen bond, while the band at 3640 cm$^{-1}$ corresponds to the absorption of a free hydroxyl group. The shoulder on the high-frequency side of the peak of the free hydroxyl group (3648 cm$^{-1}$) should probably be assigned to the manifestation of conformational effects [2], as in the case of β-phenylethanol (II).

An examination of the data on β-phenylethanols [2-4] and an investigation of the molecular models of I make it possible to suppose that the intramolecular hydrogen bond in I is formed between the hydrogen of the hydroxyl group and the π electrons of the 1,2-dihydropyrrolizine system in the region of N, C-5, and C-6.



I

A comparison of the $\Delta\nu_{OH}$ values for I (60 cm$^{-1}$) and II (29 cm$^{-1}$) [2,3] indicates greater strength of the hydrogen bond in the first case. An estimate of the energy of the hydrogen bond in I, in correspondence with [5], gives 1.7 kcal/mole, while this energy is 0.88 kcal/mole [4] for II.

The electron densities and bond orders for benzene and pyrrole presented in [6] attest to higher electron density on the carbon atoms for pyrrole and higher "multiple bond unsaturation" than is the case for benzene. Consequently, the π-hydrogen bond, under equal steric conditions, should be stronger in the pyrrole ring.

## EXPERIMENTAL

A mixture of 5- and 7-(β-hydroxyethyl)-1,2-dihydropyrrolizine [7] was treated with formaldehyde via the method in [8]. Compound I was isolated in 36% yield (based on the I in the mixture) and had bp 120-121° (2 mm) and $n_D^{20}$ 1.5412. The purity of the compound was confirmed by gas-liquid chromatography.

The IR spectra of $CCl_4$ solutions ($5 \cdot 10^{-3}$, $3 \cdot 10^{-3}$, and $2 \cdot 10^{-3}$ M) were recorded with a UR-10 spectrophotometer at room temperature.

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