The effect of the solvents on the specific intramolecular C—H...N interactions studied by ^{1}H NMR spectroscopy

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The analysis of the effect of the solvents on the proton chemical shifts in ^{1}H NMR spectra of 2-vinyloxypyridine indicates that the C—H...N interaction of weak intramolecular hydrogen bond type hinders the formation of intermolecular hydrogen C—H...X and C—H...π bonds. The protonating solvents reduce the intramolecular C—H...N interaction due to association with the N atom of the pyridine cycle.

Key words: ^{1}H NMR spectra, chemical shifts, influence of solvents; intra- and intermolecular hydrogen C—H...X bonds.

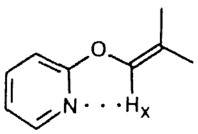
The effect of the solvents on the chemical shifts of protons is due to specific and non-specific intermolecular interactions.[1,2] In particular, the formation of a hydrogen bond with a solvent is followed by large downfield shifts of the proton signals in ^{1}H NMR spectra of the dissolved substance.[1,2] The same effect is observed if CH-acids interact with organic bases.[3,4] Previously[5—8] the specific C—H...N interactions of a weak intramolecular hydrogen bond type in the vinyl compounds were studied in detail by ^{1}H and ^{13}C NMR spectroscopy. In this work the influence of solvents on the intramolecular hydrogen C—H...N bonds in 2-vinyloxypyridine (1) and 2-methyl-4-vinyloxyquinoline (2) was studied by ^{1}H NMR spectroscopy.

Experimental

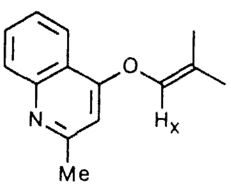
^{1}H NMR spectra were recorded on Jeol FX 90, Tesla BS 567A, and Bruker WP 200SY spectrometers (90, 100, and 200 MHz, respectively) at 25±2 °C, with $SiMe_4$ as the internal standard; concentration of substances in samples was 5 %. Deuterated solvents, HMPA, and cyclohexane were used for the registration of NMR spectra. When using non-deuterated solvents, the solvent suppression was achieved by double resonance technique.

Results and Discussion

Parameters of ^{1}H NMR spectra for compounds **1** and **2** in various solvents are listed in Table 1 and 2, respectively. Compound **1** predominantly exists in the *s-trans*-conformation with *syn*-arrangement of the N atom with respect to the vinyl group (structure **A**).[5—8]



A



B

In this case, the intramolecular hydrogen C—H...N bond is realized between the nitrogen and α-H (H_X) atoms of the vinyl group (see Refs. 5—8), resulting in a larger downfield shift of the H_X signal in the spectrum of 2-vinyloxypyridine as compared with the corresponding signal of 2-methyl-4-vinyloxyquinoline (*cf.* Tables 1 and 2). In the latter, the vinyl group also has the *s-trans*-conformation with *anti*-arrangement relative to the fused cycle[5—8] (structure **B**).

The proton chemical shifts of compounds under study in the inert solvent (cyclohexane) were chosen as the standards. The chemical shifts of all protons of the vinyl group and H(3) atom of the cycle of molecule **2** are shifted downfield (see Table 2) on going from cyclohexane to other solvents (except for benzene). Taking into account all factors causing the changes in proton chemical shifts in various solvents is a complicated problem; however, some of them can be considered. Thus, the formation of intermolecular hydrogen C—H...X bonds must result in a progressing downfield shift of the proton signals with the increasing donor ability of the solvent.[3,9]

The simplest example of such interactions is the association of chloroform with organic bases.[9—11] In this case an increase in the basicity of the solvent results in an

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increase in the chemical shift of the proton of the chloroform molecule by 2 ppm (in HMPA, see below).

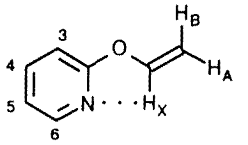
Solvent	$\delta^{9,10}$ ($\Delta\delta_{CHCl_3}$)
cyclo-C_6H_{12}	7.09
$CDCl_3$	7.24 (+0.15)
CD_3OD	7.70 (+0.61)
$(CD_3)_2CO$	7.90 (+0.81)
$(CD_3)_2SO$	8.31 (+1.22)
$(Me_2N)_3PO$	9.09 (+2.00)
C_6D_6	6.34 (−0.75)

A large upfield shift of the proton signal in benzene is due to the interaction between the proton and π-system of the benzene ring (C—H...π).[10,11] The dependence of the chemical shift of the proton of the chloroform molecule plays the role of a calibrating scale in the analysis of the influence of the solvent on the proton chemical shifts in more complex molecules. In this case, the better is the correlation between the changes of the proton chemical shifts of 2-methyl-4-vinyloxyquinoline (**2**) and those of chloroform when passing from one solvent to another one, the larger is the contribution of the intermolecular C—H...X interaction to the proton shielding constant. An analysis of ^1H NMR spectra showed that the chemical shifts of H(3) and H_X protons of compound **2** ($\Delta\delta H(3)$ and $\Delta\delta H_X$, respectively) in various solvents linearly depend on the chemical shifts of the chloroform proton ($\Delta\delta_{CHCl_3}$):

$$\Delta\delta H(3) = 0.425(\Delta\delta_{CHCl_3}) + 0.04, \quad (1)$$
$$r = 0.997,\ s = 0.09,\ n = 6;$$

$$\Delta\delta H_X = 0.477(\Delta\delta_{CHCl_3}) - 0.01, \quad (2)$$
$$r = 0.993,\ s = 0.08,\ n = 6.$$

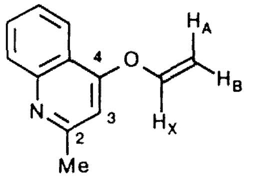
Table 1. Parameters of ^1H NMR spectra of 2-vinyloxypyridine (**1**) in various solvents



Solvent	δ (Δδ)[a]						
	H(3)	H(4)	H(5)	H(6)	H_A	H_B	H_X
cyclo-C_6H_{12}	6.67	7.47	6.79	8.08	4.34	4.77	7.77
CCl_4	6.75 (+0.08)	7.58 (+0.11)	6.89 (+0.10)	8.13 (+0.05)	4.43 (+0.09)	4.81 (+0.04)	7.70 (−0.07)
$CDCl_3$	6.78 (+0.11)	7.58 (+0.11)	6.92 (+0.13)	8.15 (+0.07)	4.47 (+0.13)	4.86 (+0.09)	7.55 (−0.22)
CD_3OD	6.83 (+0.16)	7.71 (+0.24)	7.01 (+.022)	8.13 (+0.05)	4.47 (+0.13)	4.81 (+0.04)	7.52 (−0.25)
$(CD_3)_2CO$	6.86 (+0.19)	7.77 (+0.30)	7.06 (+0.27)	8.19 (+0.11)	4.46 (+0.12)	4.80 (+0.03)	7.69 (−0.08)
$(CD_3)_2SO$	6.93 (+0.26)	7.81 (+0.34)	7.11 (+0.32)	8.21 (+0.13)	4.51 (+0.17)	4.84 (+0.07)	7.61 (−0.16)
$(Me_2N)_3PO$	6.94 (+0.27)	7.97 (+0.50)	7.18 (+0.39)	8.23 (+0.15)	4.47 (+0.13)	4.76 (−0.01)	7.70 (−0.07)
C_6D_6	6.51 (−0.16)	7.01 (−0.46)	6.45 (−0.34)	7.95 (−0.13)	4.34 (0.00)	4.87 (+0.10)	7.88 (+0.11)

[a] Here and in Table 2 the difference between the chemical shifts of the given proton in the corresponding solvent and cyclohexane (Δδ) is indicated in parentheses; the minus sign corresponds to the upfield shift of the signal, the plus sign — to the downfield shift.

Table 2. Parameters of ^1H NMR spectra of 2-methyl-4-vinyloxyquinoline (**2**) in various solvents



Solvent	δ (Δδ)			
	H(3)	H_A	H_B	H_X
cyclo-C_6H_{12}	6.52	4.54	4.94	6.65
CCl_4	6.47 (−0.05)	4.59 (+0.05)	4.98 (+0.04)	6.65 (0.00)
$CDCl_3$	6.68 (+0.16)	4.71 (+0.17)	5.08 (+0.14)	6.77 (+0.12)
CD_3OD	6.82 (+0.30)	4.80 (+0.26)	5.12 (+0.18)	6.98 (+0.33)
$(CD_3)_2CO$	6.91 (+0.39)	4.74 (+0.20)	5.08 (+0.14)	7.04 (+0.39)
$(CD_3)_2SO$	7.07 (+0.55)	4.83 (+0.29)	5.14 (+0.20)	7.20 (+0.55)
$(Me_2N)_3PO$	7.40 (+0.88)	4.80 (+0.26)	5.12 (+0.18)	7.55 (+0.90)
C_6D_6	6.21 (−0.31)	4.27 (−0.27)	4.82 (−0.12)	6.21 (−0.44)

Hence, the intermolecular hydrogen C—H...X bonds with participation of H(3) and H_X atoms are formed in molecule **2**.

Similar correlations for H_A and H_B protons were not found, *i.e.*, the non-specific interactions make substantial contribution to the shielding constants of these protons.

The same tendency is characteristic of the chemical shifts of the ring protons H(3), H(4), H(5), and H(6) of 2-vinyloxypyridine (**1**); the solvents of high basicity cause a downfield shift of the signals of indicated protons, while benzene causes an upfield shift (see Table 1). In this case a satisfactory correlation between the chemical shifts of H(4) and H(5) atoms and the $\Delta\delta_{CHCl_3}$ values was observed:

$$\Delta\delta H(4) = 0.338(\Delta\delta_{CHCl_3}) - 0.06, \quad (3)$$
$$r = 0.944,\ s = 0.25,\ n = 6;$$

$$\Delta\delta H(5) = 0.258(\Delta\delta_{CHCl_3}) - 0.01, \quad (4)$$
$$r = 0.920,\ s = 0.25,\ n = 6.$$

All ring hydrogen atoms of molecule **1** probably participate in association with the molecules of proton-acceptor solvents.

The influence of the solvent on the chemical shifts of H_A and H_B protons of 2-vinyloxypyridine is not a pronounced one, as in the case of 2-methyl-4-vinyloxyquinoline. At the same time the regularity in the change of chemical shifts of the H_X proton in compound **1** is in complete disagreement with that found for the H_X proton in compound **2**. Firstly, there is no qualitative correlation between the values of chemical shifts of H_X protons of molecule **1** and those of chloroform in various solvents, though it is strictly observed for $\Delta\delta H_X$ of molecule **2** (see Eq. (2)). Secondly, the direction of changes of the chemical shifts of H_X proton of 2-vinyloxypyridine on going from cyclohexane to other solvents was found to be opposite that for chloroform, *i.e.*, the solvents of high basicity cause an upfield shift of the H_X signal of molecule **1** by 0.1—0.2 ppm, while benzene causes a downfield one by 0.1 ppm (see Table 1).

The fundamental differences in the solvent effect on the chemical shifts of H_X atom in the spectra of compounds **1** and **2** indicate a different character of the interaction of this proton with the solvent. In molecule **2**, the H_X atom, being in the geminal position with respect to the electronegative O atom, forms effective intermolecular hydrogen bonds of C—H...X or C—H...π type with the solvent molecules. Obviously, it is not the case for 2-vinyloxypyridine. The most probable reason for this difference is the presence of the intramolecular hydrogen C—H_X...N bond in molecule **1**, which hinders the formation of the intermolecular hydrogen bonds with participation of this proton. A noticeable upfield shift of the H_X signal of 2-vinyloxypyridine in $CDCl_3$ and CD_3OD (by 0.22—0.25 ppm) is explained by association of the molecules of these solvents with the N atom of the pyridine ring, which results in a weakening of the intramolecular hydrogen C—H_X...N bond.

It is of interest that the values of the chemical shift of H_X proton in the spectra of molecules **1** and **2** in HMPA become nearly equal (7.70 and 7.55 ppm, respectively), while the difference between these values in benzene is 1.67 ppm (7.88 and 6.21 ppm, respectively). The use of solvents of high basicity impedes the investigation of intramolecular hydrogen C—H...X bonds since the spectral effects induced by this interaction are masked by effects of the intermolecular hydrogen C—H...X bonds in the model compounds.

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