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SPECIFIC C–H···N INTRAMOLECULAR INTERACTIONS IN THE VINYLOXY- AND VINYLTHIOPYRIDINE SERIES

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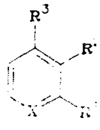
A weak hydrogen bond with the participation of the vinyl group α-hydrogen atom arises in 2-vinyloxypyridine and 2-vinylthiopyridine, which primarily exist in the s-trans-conformation, according to the ^1H and ^{13}C NMR data. This interaction does not take place in 2-vinyloxymethyl- and 2-vinyloxyethylpyridines, which primarily exist in the s-cis-conformation. The C—H...N intramolecular interaction also does not occur in o-vinyloxyaniline due to the specific features of the stereoelectronic state of the amino group nitrogen atom.

Examples of the appearance of C—H...X (X = heteroatom) specific intramolecular interactions of the weak hydrogen bond type are extremely limited [1-6]. This makes it difficult to determine the factors required for the appearance of this interaction. The parameters of the ^1H and ^{13}C NMR spectra of a systematically selected series of molecules were analyzed in the present study: 2-, 3-, 4-vinyloxypyridines (I-III), phenylvinyl ether (IV), 2-, 3,-, 4-vinylthiopyridines (V-VII), phenylvinyl sulfide (VIII), 2-, 3-, 4-vinyloxymethylpyridines (IX-XI), benzylvinyl ether (XII), 2-vinyloxyethylpyridine (XIII), and *o*-, *m*-, *p*-vinyloxyanilines (XIV-XVI). Compounds VI and VII were synthesized for the first time.



I-XVI

I, IV, XIV $R^1=OCH=CH_2$, $R^2=R^3=H$; II, XV $R^1=R^3=H$, $R^2=OCH=CH_2$; III, XVI $R^1=R^2=H$, $R^3=OCH=CH_2$; V, VIII $R^1=SCH=CH_2$, $R^2=R^3=H$; VI $R^1=R^3=H$; $R^2=SCH=CH_2$; VII $R^1=R^2=H$, $R^3=SCH=CH_2$; IX, XII $R^1=CH_2OCH=CH_2$, $R^2=R^3=H$; X $R^1=R^3=H$, $R^2=CH_2OCH=CH_2$; XI $R^1=R^2=H$, $R^3=CH_2OCH=CH_2$; XIII $R^1=C_2H_4OCH=CH_2$, $R^2=R^3=H$; I—III, V—VII, IX—XI, XIII X=N; IV, VIII, XII X=CH; XIV—XVI $X=CNH_2$

The parameters of the ^1H and ^{13}C NMR spectra (see Table 1) of the vinyl group in the series of vinyl ethers and sulfides are a function of the intensity of *p*—π conjugation in the vinyloxy(vinylthio) group [7, 8]. The intensity of *p*-π conjugation in the vinyloxy group of aryl-and hetarylvinyl ethers and sulfides is a function of the conditions of competitive *p*—π conjugation with an unsaturated fragment [7-9]. The chemical shift of the β-carbon atom of the vinyl group is the criterion of efficiency of *p*—π conjugation [9]. The character of the change in the position of the signal of the $C_{(\beta)}$ atom in vinylthiopyridines V-VII and phenylvinyl sulfide VIII is the same as in vinyloxypyridines I-III and phenylvinyl ether IV. The nucleus of the $C_{(\beta)}$ atom in phenylvinyl ether IV (95.1 ppm) and sulfide VIII (115.3 ppm) is most shielded. The resonance of this nucleus is successively shifted to the weak field in going to 2-vinyloxy(vinylthio)-, 3-vinyloxy(vinylthio)-, and 4-vinyloxy(vinylthio)pyridines (I-III, V-VII), respectively (see Table 1).

The chemical shifts of the vinyl group β-protons ($H_{(A)}$ and $H_{(B)}$) in ethers I-IV and sulfides V-VIII change symbatically with the chemical shift of the $C_{(\beta)}$ atom. The region of their change in these groups of compounds does not exceed 0.3 ppm, and the relative chemical shift of the $H_{(A)}$ and $H_{(B)}$ protons ($\Delta\delta = \delta H_{(A)} - \delta H_{(B)}$) for ethers

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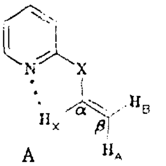
TABLE 1. ^1H and ^{13}C NMR Spectra of Derivatives of Pyridine I-III, V-VII, IX-XI, XIII, Benzene IV, VIII, XII, and Aniline XIV-XVI

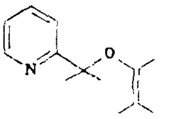
Compound	Chemical shift, δ, ppm						SSCC, J, Hz		
	$H_{(A)}$	$H_{(B)}$	$H_{(X)}$	Δδ	$C_{(\alpha)}$	$C_{(\beta)}$	$^1J\ C_\beta H_A$	$^1J\ C_\beta H_B$	$^1J\ C_\alpha H_X$
I	4,49	4,87	7,55	0,38	144,17	95,21	162,1	157,9	188,3
II	4,51	4,81	6,62	0,30	147,48	96,72	162,5	158,5	184,1
III	4,69	5,00	6,68	0,31	145,09	99,53	162,5	158,9	186,0
IV	4,40	4,74	6,62	0,34	148,37	95,07	161,8	157,9	182,5
V	5,49	5,56	7,11	0,07	128,17	116,33	161,9	159,0	178,5
VI	5,43	5,37	6,50	−0,06	130,42	117,07	161,8	159,5	174,5
VII	5,64	5,68	6,57	0,04	126,98	121,93	161,6	160,0	175,8
VIII	5,33	5,31	6,52	−0,02	131,92	115,33	161,4	159,3	173,3
IX	4,08	4,30	6,58	0,22	151,43	87,90	161,5	156,4	182,5
X	4,12	4,30	6,55	0,18	151,32	87,79	161,6	156,2	182,5
XI	4,13	4,28	6,58	0,15	151,88	88,08	161,9	156,3	183,1
XII	4,04	4,27	6,52	0,23	151,66	87,34	161,4	156,4	181,6
XIII	3,96	4,18	6,41	0,22	151,63	86,66	161,1	156,1	181,1
XIV	4,35	4,65	6,57	0,30	148,96	93,76	161,4	157,7	184,1
XV	4,36	4,72	6,57	0,36	148,25	94,86	161,8	157,7	182,8
XVI	4,27	4,58	6,56	0,31	149,97	92,97	161,7	157,5	182,2

I-IV is in the region of 0.30-0.38 ppm. This indicates the existence of molecules I-IV primarily in the *s-trans*-conformation A [10]. For 2- and 4-vinylthiopyridines (V, VII), Δ*δ* = 0.04-0.07 ppm, which is also in agreement with the predominant *s-trans*-conformation of these sulfides [11]. The Δ*δ* decreases to −0.02 to −0.06 ppm in 3-vinylthiopyridine VI and phenylvinyl sulfide VIII, which probably reflects an increase in the population density of the *s-cis*-form.

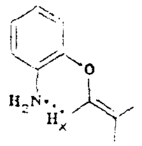
The chemical shifts of the vinyl group α-protons ($H_{(X)}$) in 3-, 4-vinyloxypyridines (II, III), phenylvinyl ether (IV), as in 3-, 4-vinylthiopyridines (VI, VII) and phenylvinyl sulfide VIII, differ little (<0.1 ppm). In going to 2-vinyloxypyridine I and 2-vinylthiopyridine V, the resonance of the $H_{(X)}$ proton is unevenly shifted to the weak field by 0.9 and 0.6 ppm, respectively. The observed change is due to a specific interaction of the weak hydrogen bond type between the α-hydrogen atom of the vinyl group and the endocyclic nitrogen atom [1-6]. This interaction occurs in 2-vinyloxy- and 2-vinylthiopyridines (I, V) in the *s-trans*-conformation in the *syn*-position of the nitrogen atom and vinyl group (structure A).



A



B



C

X=O, S

The weaker field shift of the $H_{(X)}$ signal in 2-vinyloxypyridine I indicates the higher intensity of the interaction of O−C−H···N than C−H···N.

In agreement with the general tendency toward a change in the chemical shifts of $C_{(\alpha)}$ and $C_{(\beta)}$ atoms in vinyl ethers [7] and sulfides [8], the chemical shifts of these atoms in compounds II-IV, as in compounds VI-VIII, change antibatically. A strong-field shift in the signal of the $C_{(\alpha)}$ atom corresponds to a weak-field shift of the signal of the $C_{(\beta)}$ atom in the series of compounds IV, II, and III. The decrease in the chemical shift of the $C_{(\alpha)}$ atom corresponds to an increase in the chemical shift of the $C_{(\beta)}$ atom in the series of VIII, VI, and VII (see Table 1). Based on the observed character of the change in the chemical shifts of the $C_{(\alpha)}$ and $C_{(\beta)}$ atoms in molecules II-IV, VI-VIII, and the data in [7, 8], it could be predicted that the chemical shifts of the $C_{(\alpha)}$ atom in 2-vinyloxy- (I) and 2-vinylthiopyridines (V) have values intermediate between those for ethers II, IV and sulfides VI, VIII. However, the nucleus of the $C_{(\alpha)}$ atom is 3-4 ppm more shielded in the first case and 2-3 ppm more shielded in the second case (see Table 1). An additional contribution to the shielding constant of the $C_{(\alpha)}$ nuclei in vinylpyridines I, V is the consequence of the specific interaction of $C_{(\alpha)}$—$H_{(X)}$···N [7, 8].

The lines of the ^{13}C—^1H SSCC involving the β-carbon of the vinyl group ($^1J_{C_\beta H_A}$ and $^1J_{C_\beta H_B}$) in the series of vinyl ethers I-IV and sulfides V-VIII vary within narrow limits (≤1 Hz, Table 1). The line of the ^{13}C—^1H SSCC involving the α-carbon atom of the vinyl group ($^1J_{C_\alpha H_X}$) undergoes significantly greater changes in these compounds, and the correlation of the change in the values of ${}^1J_{C_\alpha H_X}$ and $\delta_{C_{(\beta)}}$, well-known for a wide range of vinyl ethers [7] and sulfides [8], is observed. The ${}^1J_{C_\alpha H_X}$ SSCC in phenyl ether IV and 3-, 4-vinyloxypyridines II and III thus increases symbatically to the chemical shift of the $C_{(\beta)}$ atom (182.5, 184.1, 186.0 Hz, respectively). A similar increase in the ${}^1J_{C_\alpha H_X}$ SSCC occurs in phenylvinyl sulfide VIII and 3-, 4-vinylthiopyridines VI and VII (see Table 1). On this basis, we hypothesized a value of the ${}^1J_{C_\alpha H_X}$ SSCC in 2-vinyloxypyridine I intermediate between ethers II and IV and a value of ${}^1J_{C_\alpha H_X}$ in 2-vinylthiopyridine IV intermediate between sulfides VI and VIII. Actually, the ${}^1J_{C_\alpha H_X}$ SSCC in 2-vinyloxypyridine I increases by 4-6 Hz relative to the SSCC of compounds II and IV, and this SSCC is 3-5 times higher in 2-vinylthiopyridine V than the SSCC of compounds VI and VIII. As a consequence, an additional positive contribution to the ${}^1J_{C_\alpha H_X}$ SSCC due to the specific $C_{(\alpha)}$—$H_{(X)}$...N interaction occurs in 2-vinylpyridines I and V [6-8].

Let us compare the spectral characteristics of the vinyl group in compounds IX-XI, XIII, and XII. As the data in Table 1 show, the parameters of the ${}^1H$ and ${}^{13}C$ NMR spectra virtually do not change regardless of the position of the axial vinyloxy group in the pyridine ring (molecules IX-XI) or the absence of an endocyclic nitrogen atom (ether XII). Lengthening of the alkyl chain separating the 2-substituted pyridine ring and vinyloxy group (compounds IX and XIII) also does not cause any significant changes in the spectral parameters (see Table 1).

It is necessary to analyze the spatial and electronic structure of ethers IX-XIII in order to understand the cause of the lack of spectral anomalies for 2-vinylpyridines IX and XIII. The signal of the $C_{(\beta)}$ atom in vinyloxymethylpyridines IX-XI and benzylvinyl ether XII is shifted by 7-11 ppm to the strong field relative to the signals of the corresponding vinyloxypyridines I-III and phenylvinyl ether IV. This shift is due to loss of competitive $p—\pi$ conjugation with the aryl (hetaryl) ring because of incorporation of a methylene bridge between the vinyloxy group and the unsaturated cyclic fragment [10]. There are no significant changes in the chemical shift of the $C_{(\beta)}$ atom with a change in the position of the vinyloxymethyl group in the pyridine ring (compounds IX-XI, Table 1).

The relative chemical shift of the vinyl group β-protons ($\Delta\delta = \delta_{H_{(A)}} - \delta_{H_{(B)}}$) in vinyl ethers IX-XIII is 0.15-0.22 ppm, which indicates the existence of these ethers primarily in the *s-cis*-conformation (structure B) [10].

The $H_{(X)}$ hydrogen atom is spatially distant from the endocyclic nitrogen atom and the specific $C_{(\alpha)}$ — $H_{(X)}\cdots$N interaction does not take place with such a spatial structure of compounds IX and XIII. This is why there are no weak-field shift of the $H_{(X)}$ signal, additional contributions to the shielding constant of the $C_{(\alpha)}$ atom and ${}^1J_{C_\alpha H_X}$ SSCC in going from vinyloxymethylpyridines X, XI and benzylvinyl ether XII to vinylpyridines IX, XIII.

A specific interaction between the nitrogen atom of the NH_2 group and the $H_{(X)}$ hydrogen atom (structure B) is potentially possible for *o*-vinyloxyaniline XIV. In the series of vinyloxyanilines XIV-XVI, pronounced variations of the chemical shift of the $C_{(\beta)}$ atom take place with a change in the relative position of the NH_2 and $OCH{=}CH_2$ groups. The chemical shifts of the $H_{(A)}$ and $H_{(B)}$ atoms change symbatically with the chemical shift of the $C_{(\beta)}$ atom, but the position of the $H_{(X)}$ proton resonance remains almost constant (6.56-6.57 ppm). The change in the chemical shifts of the $C_{(\alpha)}$ and $C_{(\beta)}$ atoms in the series of vinyloxyanilines XIV-XVI is antibatic. The strong-field shift in the signal of the $C_{(\alpha)}$ atom corresponds to a successive weak-field shift in the signal of the $C_{(\beta)}$ atom for *p*-, *o*-, and *m*-vinyloxyanilines (XVI, XIV, XV, respectively) (see Table 1). No additional contribution to shielding of the $C_{(\alpha)}$ atom is observed for *o*-vinyloxyaniline (XIV).

A slight increase in the ${}^1J_{C_\alpha H_X}$ is observed in *o*-vinyloxyaniline XIV in comparison to the SSCC of *m*- and *p*-vinyloxyanilines XV and XVI (1-2 Hz, see Table 1). A similar increase in the ${}^1J_{C_\alpha H_X}$ SSCC is observed when the substituent in the aryl ring is a π donor, but a strong σ acceptor [7]. The ${}^1H$ and ${}^{13}C$ NMR data indicate the absence of a $C_{(\alpha)}$—$H_{(X)}\cdots$N interaction in *o*-vinyloxyaniline XIV.

The endocyclic nitrogen atom (in the pyridine ring), in contrast to the exocyclic atom (in the NH_2 group), thus becomes capable of the specific C—H$\cdots$N interaction in the corresponding steric conditions. A difference in the stereoeletronic state of the unshared electron pairs in these atoms could be the cause of the observed differences. For the "pyridine" nitrogen atom, the unshared electron pair is sp^2-hybridized and localized on the nitrogen atom [12], which allows the electrons in the unshared pair to participate in the specific interaction discussed. The unshared electron pair for the NH_2 group nitrogen atom is sp^3-hybridized and delocalized to the π system of the aromatic fragment [13, 14], which impedes its participation in the nonvalent interaction.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Tesla BS-497 spectrometer (100 MHz), and the ^{13}C NMR spectra were recorded on Tesla BS-567A (25.1 MHz) and Bruker WP 200 SY spectrometers (50.33 MHz). The solvent was $CDCl_3$ and the internal standard was HMDS. The concentration of the samples was 5% for ^1H NMR and 30% for ^{13}C NMR. The $^{13}C—^1H$ SSCC lines were measured with the gated decoupling method in [15].

3-Vinylthiopyridine (VI). A 0.5-liter autoclave was filled with 16.6 g (150 mmole) of 3-mercaptopyridine, 3.4 g (60 mmole) of KOH, 80 ml of dioxane, and 3 ml of water, and acetylene was delivered under 15 atm. The reaction mass was heated for 1 h at 180°C and 9.1 g (44%) of vinylthiopyridine VI with T_b of 87-89°C (12 mm Hg), n_D^{20} 1.5760, d_4^{20} 1.1004, was separated by vacuum fractional distillation.

4-Vinylthiopyridine (VII) was prepared similar to compound VI by vinylation of 11.1 g (100 mmole) of 4-thiopyridone in the presence of 3.4 g (60 mmole) of KOH in a solution of aqueous dioxane with a yield of 9.0 g (65%); T_b 92-93°C (10 mm Hg), n_D^{20} 1.6021, d_4^{20} 1.1192.

The other vinylthio- and vinyloxypyridines were prepared by the methods in [16, 17].

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