Specific intramolecular C—H...O interactions in 1-vinyl-2-formylimidazole and 1-vinyl-2-formylbenzimidazole studied by ^1H and ^{13}C NMR spectral data

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According to the ^1H and ^{13}C NMR spectral data, the vinyl group in 1-vinyl-2-formylimidazole and 1-vinyl-2-formylbenzimidazole is *trans*-oriented with respect to the formyl fragment, while the carbonyl group occupies the *anti*-position with respect to the N atom of pyridine cycle. A specific intramolecular C—H...O interaction of a weak hydrogen bond type is realized between the α-H atom of the vinyl group and O atom of the carbonyl group.

Key words: 1-vinyl-2-formylimidazole, 1-vinyl-2-formylbenzimidazole, specific intramolecular C—H...O interaction; ^1H and ^{13}C NMR spectra.

Structural investigations of a large series of 1-vinylimidazoles based on ^1H and ^{13}C NMR spectral data showed the presence of specific intramolecular interactions (SII) in several molecules.[1–3] Thus, in 1,1′-divinyl-, 1-vinyl-2,2′-biimidazolyls, and 1-vinyl-2,2′-pyridylbenzimidazole the specific intramolecular C—H...N interactions of a weak hydrogen bond type between the α-H atom of the vinyl group and the endocyclic N atom were found.[2] This is in agreement with the data of the crystallographic study.[4] The spatial structure of coordination compounds of 1,1′-divinyl-2,2′-biimidazolyl was established on the basis of spectral effects caused by SII.[5] In the present work 1-vinyl-2-formylimidazole and 1-vinyl-2-formylbenzimidazole were synthesized and the structures of these compounds were studied.

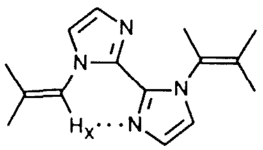
Experimental

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker WP 200 SY spectrometer operating at 200 and 50.3 MHz, respectively, with HMDS as the internal standard. Concentrations of substances in samples for ^1H and ^{13}C NMR were 5 % and 30 %, respectively. To analyze the spin systems in proton-coupled ^{13}C NMR spectra a standard procedure[1] was used.

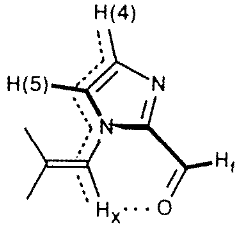
1-Vinyl-2-formylimidazole and 1-vinyl-2-formylbenzimidazole were synthesized by oxidation of the corresponding 1-vinyl-2-hydroxymethylimidazoles by MnO_2 in dioxane.[6]

Results and Discussion

The parameters of ^1H and ^{13}C NMR spectra for 1-vinylimidazoles **1—10** are listed in Table 1. The signals of β-protons of the vinyl group (H_A and H_B) in the spectrum of 1-vinyl-2-formylimidazole (**1**) are shifted slightly downfield (by 0.1—0.3 ppm) with respect to corresponding signals for 1-vinylimidazoles **2—8**; it is caused by a decrease in the p—π-conjugation due to the electron acceptor effect of the formyl group.[7] A considerably larger downfield shift is characteristic of α-protons of the vinyl group (H_X) in compound **1** as well as of those in 1-vinyl- and 1,1′-divinylbiimidazolyls **9** and **10** (see Table 1). It is associated with the specific intramolecular C—H_X...N interactions if the imidazole cycles are *anti*-oriented and the vinyl groups, in turn, are in the *trans*-position to the former[2] (structure **A**).



A



B

An estimate of the contribution of the anisotropy of carbonyl group to the shielding constant of H_X proton calculated by the McConnell formula for related 1-vinyl-2-formylimidazole molecules does not explain the downfield shift of the H_X signal solely by the effect of carbonyl group anisotropy.[8,9] Furthermore, H_X and N atoms of the second imidazole cycle in biimidazolyls **9** and **10** are separated by the same number of bonds as the

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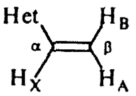
Table 1. Parameters of ^{1}H and ^{13}C NMR spectra of *N*-vinylimidazoles **1—22**



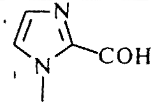
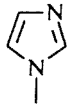
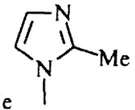
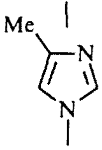
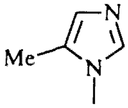
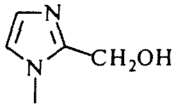
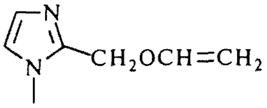
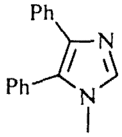
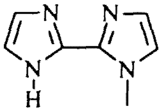
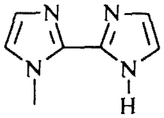
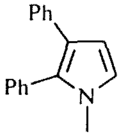
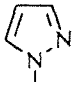
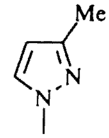
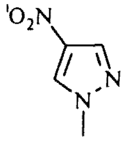
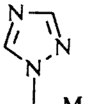
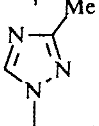
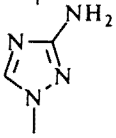
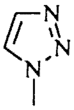
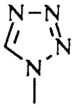
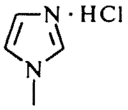
Compound	Het	δ ^{1}H			δ ^{13}C		J/Hz		
		H$_A$	H$_B$	H$_X$	C(α)	C(β)	$^1J_{C(\beta),H_A}$	$^1J_{C(\beta),H_B}$	$^1J_{C(\alpha),H_X}$
1		5.08	5.40	7.92	129.92	105.30	164.9	157.6	187.8
2		4.83	5.24	6.88	129.51	101.72	164.9	157.5	178.0
3		4.84	5.15	6.89	128.87	101.98	164.5	157.5	176.5
4		4.79	5.16	6.81	129.51	100.52	164.9	157.5	177.2
5		4.95	5.30	6.76	127.49	103.96	164.4	157.7	177.9
6		4.85	5.19	7.14	129.14	102.87	—	—	*
7		4.89	5.23	7.01	128.87	102.80	164.2	157.5	178.9
8		4.88	5.34	6.54	129.73	103.67	164.6	158.0	179.4
9		4.98	5.29	8.51	130.63	102.18	164.5	157.0	185.5
10		4.92	5.25	8.06	131.18	101.86	164.2	157.2	184.4
11		4.57	5.04	6.75	133.28	96.94	164.0	156.6	173.3
12		4.58	5.11	6.68	131.64	98.14	164.1	157.1	176.7
13		4.76	5.43	7.00	133.11	99.53	163.9	159.3	177.9

Table 1 (continued)

Compound	Het	δ ^1H			δ ^{13}C		J/Hz		
		H_A	H_B	H_X	C(α)	C(β)	$^1J_{C(\beta),H_A}$	$^1J_{C(\beta),H_B}$	$^1J_{C(\alpha),H_X}$
14		4.66	5.35	6.88	131.77	96.83	163.6	158.7	176.7
15		5.12	5.76	7.01	132.20	105.53	165.4	160.8	183.4
16		4.98	5.71	7.07	129.39	104.07	164.7	161.3	181.1
17		4.99	5.70	6.98	128.98	103.27	164.3	161.0	180.0
18		4.86	5.55	6.83	128.68	101.57	163.9	161.1	178.2
19		5.16	5.52	6.96	126.82	105.90	165.2	158.5	182.4
20		5.18	5.70	7.38	130.29	105.23	165.7	160.0	183.8
21		5.44	6.01	7.36	126.71	109.49	166.0	161.6	187.7
22		5.39	5.82	7.48	128.36	109.02	166.0	159.3	187.4

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* Spin-spin coupling constants $^{13}C—^1H$ were not determined because of the low solubility of the specimen.

H_X and O atoms of the carbonyl group in formylimidazole **1** (*cf.* structures **A** and **B**). Therefore, the anomalous downfield shift of the H_X signal in the spectrum of compound **1** is evidence of the presence of the specific intramolecular C—H...O interactions between the H_X and O atoms of the carbonyl group. For realization of such an interaction the vinyl group must be *trans*-oriented relative to the formyl one, while the carbonyl group must occupy the *anti*-position relative to the N(3) atom (see structure **B**).

One can obtain independent information about the spatial structure of compound **1** from the analysis of the long-range spin-spin interactions between protons. Two types of the $^1H—^1H$ interaction through 5 bonds were found in molecule **1**: between H_X—H(4) protons ($^5J_{H(4),H_X}$ = 0.55 Hz) and between H(5)—H_f protons ($^5J_{H(5),H_f}$ = 1.0 Hz) (see structure **B**). At the same time no interaction between H(4) and H_f protons was found. Each of these interactions is transferred through a near-planar zigzag-shaped fragment.[10,11] Hence, the vinyl group must have

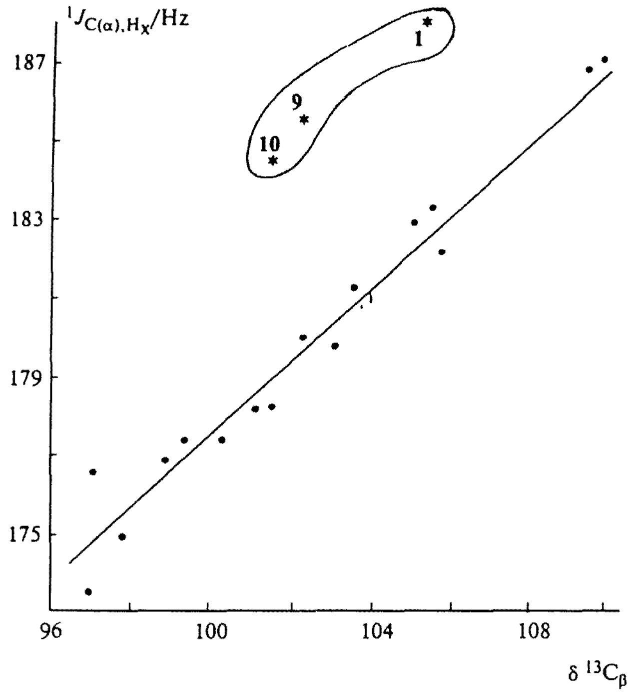


Fig. 1. Dependence of the spin-spin coupling constants $^1J_{C(\alpha),HX}$ on the chemical shifts $\delta\ ^{13}C(\beta)$ in the spectra of *N*-vinylazoles **2**, **4**, **8**, **11—22**. Experimental data for compounds **1**, **9** и **10** are marked by asterisks.

the *trans*-orientation with respect to the formyl group, while the carbonyl group must be *anti*-oriented relative to the N(3) atom (see structure **B**).

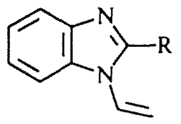
An increase in spin-spin coupling constant $^{13}C—^1H$ (see Refs. 12 and 13) is another reliable sign of the presence of the specific intramolecular C—H...O interactions. In the case of compound **1** the value of the spin-spin coupling constant $^1J_{C(\alpha),H_X}$ is about 8—10 Hz larger then those for molecules **2—8**. Similar values of the spin-spin coupling constant $^1J_{C(\alpha),H_X}$ are only observed for biimidazolyls **9** and **10**. In this case the range of changes of the $^1J_{C(\beta),H_A}$ and $^1J_{C(\beta),H_B}$ constants for imidazoles **1—10** does not exceed 1 Hz (see Table 1). To make a quantitative estimation of additional contribution to the spin-spin coupling constant $^1J_{C(\alpha),H_X}$ due to the specific intramolecular C—H...O interactions in formylimidazole **1** one must consider their values for a large series of vinylazoles (**2**, **4**, **8**, **11—22**). A correlation, usual for vinyl derivatives, between the spin-spin coupling constant $^1J_{C(\alpha),H_X}$ and the chemical shifts of β-C atom of the vinyl group ($\delta\ ^{13}C(\beta)$)[13,14] is observed in the spectra of compounds **2**, **4**, **8**, **11—22**:

$$^1J_{C(\alpha),H_X} = 0.884[\delta\ ^{13}C(\beta)] + 89.31, \qquad (1)$$
$$r = 0.970,\ s = 0.28,\ n = 15.$$

The value of the spin-spin coupling constant $^1J_{C(\alpha),H_X}$ in formylimidazole **1** deviates from that calculated with Eq. (1) by 5.4 Hz (Fig. 1) and serves as a quantitative estimate of the contribution of the specific intramolecular C—H...O interactions to the spin-spin coupling constant $^1J_{C(\alpha),H_X}$. It is confirmed by *ab initio* quantum-chemical calculations.[15] Nearly the same deviation of $^1J_{C(\alpha),H_X}$ value from that calculated with Eq. (1) is observed for biimidazolyls **9** and **10** (5.9 and 5.0 Hz, respectively, see Fig. 1). Hence, the specific intramolecular C—H...O interactions in formylimidazole **1** and C—H...N in divinylbiimidazolyls **9** and **10** are comparable.

The parameters of ^1H and ^{13}C NMR spectra for 2-substituted 1-vinylbenzimidazoles **23—32** are listed in

Table 2. Parameters of ^1H and ^{13}C NMR spectra of *N*-vinylbenzimidazoles **23—32**



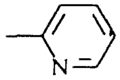
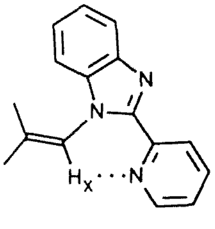
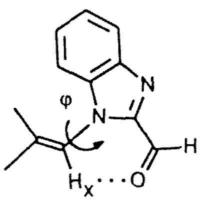
Compound	R	δ ^1H			δ $^{13}C(\beta)$	*J*/Hz		
		H_A	H_B	H_X		$^1J_{C(\beta),H_A}$	$^1J_{C(\beta),H_B}$	$^1J_{C(\alpha),H_X}$
23	C(O)H	5.36	5.61	7.76	108.37	163.4	158.8	184.8
24	Me	5.14	5.43	6.90	105.74	162.9	158.1	176.0
25	Et	5.17	5.47	6.92	106.16	163.0	158.3	175.4
26	CH_2OH	5.17	5.52	7.13	107.67	163.2	159.4	178.9
27	$CH_2OCH=CH_2$	5.18	5.53	7.09	106.54	163.0	169.1	178.7
28	CH_2Ph	5.10	5.41	6.83	106.87	163.2	159.1	177.3
29	SMe	5.20	5.55	6.96	106.13	163.7	158.9	176.8
30	$SCH=CH_2$	5.24	5.55	6.96	107.11	163.6	159.2	177.7
31	Ph	5.25	5.58	7.02	107.37	162.9	158.1	176.3
32	 N	5.28	5.56	7.96	106.34	162.7	158.3	184.7

Table 2. Spectral effects similar to those for compound **1** are observed for 1-vinyl-2-formylbenzimidazole **23**. The signal of the H_X proton in the spectrum of compound **23** is characterized by a larger downfield shift (by 0.6—0.9 ppm), while the signals of H_A and H_B protons are slightly shifted downfield (by 0.1—0.2 ppm, see Table 2) as compared with those for other benzimidazoles (**24—31**). The value of the spin-spin coupling constant ${}^1J_{C(\alpha),H_X}$ for formylbenzimidazole **23** is by 6—9 Hz larger than those for benzimidazoles **24—31** while the values of constants ${}^1J_{C(\beta),H_A}$ and ${}^1J_{C(\beta),H_B}$ virtually do not differ. In the spectra of formylbenzimidazole **23** the values of the chemical shift and the spin-spin coupling constant ${}^1J_{C(\alpha),H_X}$ for the H_X proton are close to that for 1-vinyl-2,2′-pyridylbenzimidazole (**32**) (see Table 2). In the latter molecule the specific intramolecular C—H...N interaction is realized between the H_X atom and the nitrogen atom of pyridine ring (structure **C**).



C



D

Taking into account the similarity in the spectral manifestations of both C—H...N and C—H...O SII, one can assume that in 1-vinyl-2-formylbenzimidazole **23** the specific intramolecular C—H...O interaction is also realized. To this end, it is necessary that the vinyl group would have the *trans*-orientation with respect to the formyl group, while the carbonyl group should be in the *anti*-position to the N atom (structure **D**), analogously to that in the structure of compound **1**.

The difference between the spatial structure of 1-vinyl-2-formylimidazole and 1-vinyl-2-formylbenzimidazole lies in a deviation of the vinyl group out of the heterocycle plane in the latter compound. Thus, the difference between the values of the spin-spin coupling constants ${}^1J_{C(\beta),H_A}$ and ${}^1J_{C(\beta),H_B}$ (ΔJ) is 7.3 Hz for formylimidazole **1**, while it is 4.5 Hz for formylbenzimidazole **23** (see Tables 1 and 2). A decrease in the parameter ΔJ in the case of compound **23** is associated with an increase in the torsion angle φ about the N—C(α) bond (see structure **D**) compared with that found for compound **1**.[16,17]

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