Comparison of the effects of the intra- and intermolecular hydrogen bonds C—H...X (X = O, N) in ^1H and ^{13}C NMR spectra

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A similarity between manifestations of the effects of the intra- and intermolecular hydrogen bonds C—H...X (X = O, N) in ^1H and ^{13}C NMR spectra has been shown. A correlated increase in the direct spin-spin coupling constant $^{13}C-^1H$ and the chemical shifts of the proton participating in the interaction has been observed.

Key words: intra- and intermolecular hydrogen bonds C—H...X; ^1H and ^{13}C NMR spectra.

The interaction between CH-acids and organic bases, resulting in the formation of intermolecular C—H...X type hydrogen bonds, is well studied.[1,2] It is accompanied by several spectral effects, such as the anomalous downfield shift of the signal of the hydrogen atom involved in the interaction in the ^1H NMR spectrum,[3] the low-frequency shift of the absorption band of the stretching vibrations of the C—H bond in the IR spectrum,[4] an increase in the corresponding direct spin-spin coupling constant $^{13}C-^1H$.[5] Intramolecular hydrogen bonds C—H...X have been much less studied. Their formation also causes a downfield shift of the signal of the interacting hydrogen atom in the ^1H NMR spectra and an increase in the corresponding direct spin-spin coupling constant $^{13}C-^1H$.[6,7] The interpretation of IR spectral data was found to be more complicated, since the effect of the intramolecular hydrogen bonds C—H...X on the stretching vibrations of the C—H bond is masked by other intramolecular effects.[8] The aim of the present work is to compare the effects caused by both intra- and intermolecular hydrogen bonds C—H...X on ^1H and ^{13}C NMR spectra.

Experimental

^1H and ^{13}C NMR spectra of compounds **1—14** (Table 1) were recorded on Tesla BS-567A (100 and 25.1 MHz, respectively) and Bruker WP-200-SY (200 and 50.3 MHz, respectively) spectrometers in $CDCl_3$ under identical conditions. The concentrations of substances in samples were 5 % and 30 %, respectively; the accuracy of measurements of the spin-spin coupling constant $^{13}C-^1H$ was ±0.1 Hz.

Results and Discussion

The most studied example of the formation of intermolecular C—H...X hydrogen bonds is the interaction between chloroform and organic bases (B), which reveals itself as a downfield shift of the signal of the chloroform proton in the ^1H NMR spectrum and an increase in the direct spin-spin coupling constant $^{13}C-^1H$ [5] (Table 2). In this case the stronger bases form the stronger intermolecular hydrogen bonds. An increase in the interaction manifests itself as an additional downfield shift of the chloroform proton and a simultaneous increase in the direct spin-spin coupling constant $^{13}C-^1H$ (ΔJ, see Table 2). The measure of the change is the difference between the values of the corresponding chemical shift in solvent B and in cyclohexane ($\Delta\delta$). A linear dependence between $\Delta\delta$ and ΔJ according to Eq. (1) was found.

$$\Delta J = 5.96\Delta\delta + 1.91,\ r = 0.96,\ s = 0.95,\ n = 9 \qquad (1)$$

A comparison of the spectral manifestations of the intramolecular C—H...X hydrogen bonds and those of the intermolecular hydrogen bonds is hindered by the complicated relationships between the NMR spectral parameters and the spatial and electronic structures of molecules. Therefore, a careful selection of the substances to be compared is necessary, since they must satisfy two principal criteria: they must be conformationally homogeneous and have a similar electronic structure. The following pairs of compounds meet the above criteria: **1** and **2**, **3** and **4**, **6** and **7**, **8** and **9**, **9** and **10**, **11** and **12**, **13** and **14** (see Refs. 9—13). *N*-Vinylformanilide (**5**) exists as a mixture of two rotamers. For both of them (because of the hindered rotation about the amide bond) NMR spectra are recorded at room temperature.[14] In molecules **1**, **3**, and **5a** C—H...O interaction occurs, and in compounds **8**, **10**, **11**, and **13** C—H...N interaction involving the α-proton (H_X) of the vinyl group[9—14] occurs (structures **A**, **B**, and **C**).

The additional contribution of the C—H...X interactions to the corresponding shielding constant and the

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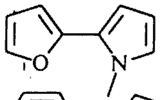
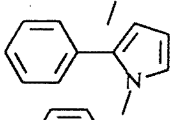
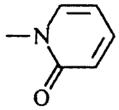
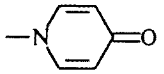
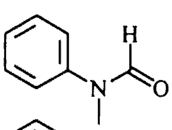
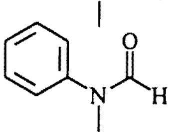
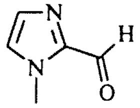
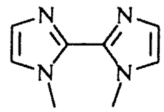
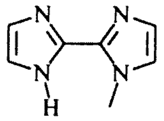
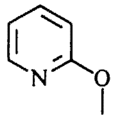
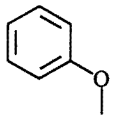
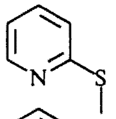
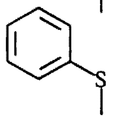
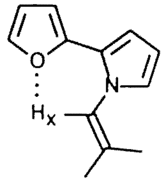
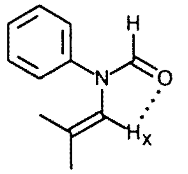
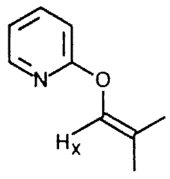
Table 1. Parameters of the ^1H and ^{13}C NMR spectra of compounds **1**—**14**

$R—C(\alpha)H_X=CH_2$

Compound	R	δH_X	$\Delta\delta$	$^1J_{C(\alpha),H_X}$ /Hz	ΔJ /Hz
1		7.12	0.27	177.3	1.5
2		6.85	—	175.8	—
3		7.50	0.79	184.7	4.0
4		6.71	—	180.7	—
5a		7.43	0.63	178.5	4.6
5b		6.80	—	173.9	—
6		7.92	0.96	187.8	5.4
7		6.96	—	182.4	—
8		8.06	1.18	184.4	6.4
9		6.88	—	178.0	—
10		8.51	1.63	185.5	7.5
11		7.55	0.98	188.3	5.8
12		6.57	—	182.5	—
13		7.11	0.59	178.5	4.9
14		6.52	—	173.6	—


A


B


C

direct spin-spin coupling constant $^{13}C—^1H$ are characterized by the difference between the chemical shifts of the H_X proton in the ^1H NMR spectra of the compared compounds ($\Delta\delta$) and by the difference between the spin-spin coupling constants $^1J_{C(\alpha),H_X}$ (ΔJ), respectively. A linear correlation between $\Delta\delta$ and ΔJ is described by Eq. (2)

$$\Delta J = 4.31\Delta\delta + 1.07,\ r = 0.95,\ s = 0.55,\ n = 8, \qquad (2)$$

where the coefficient at $\Delta\delta$ is smaller than that in Eq. (1). This difference can be explained within the

Table 2. Chemical shifts in ^1H NMR spectra and spin-spin coupling constants $^{13}C—^1H$ of $CHCl_3$ in the system chloroform—base (B)

B	$\delta\ ^1H$	$\Delta\delta$	$^1J_{C,H}$/Hz	ΔJ/Hz
C_6H_{12}[a]	7.09	—	208.1	—
$CHCl_3$[a] (pure)	7.24	0.15	209.5	1.4
$MeNO_2$[b]	7.47	0.38	213.6	5.5
Et_2O[b]	7.70	0.61	213.7	5.6
MeOH[b]	7.70	0.61	214.3	6.2
Me_2CO[b]	7.90	0.81	215.2	7.1
Et_3N[b]	8.06	0.97	214.2	6.1
$Et_2NC(O)H$[b]	8.27	1.18	217.4	9.3
Me_2SO[a]	8.31	1.22	217.7	9.6
$(Me_2N)_3PO$[a]	9.09	2.00	221.7	13.6

[a] Ref. 5. [b] Ref. 3.

framework of the electrostatic model of the hydrogen bond.[15] According to Buckingham's theory the effect of the electric field on the shielding constant is described by an approximate equation:[16]

$$\Delta\delta = -AE_z - BE^2, \quad (3)$$

where E_z is the electric field component along the direction of the C—H bond, and E^2 is the squared electric field strength at the proton.

The second term in Eq. (3) does not depend on the spatial orientation of the C—H bond relative to the unshared electron pair of the heteroatom. At the same time, the effect of the C—H...X interaction on the spin-spin coupling constant ^{13}C—^{1}H is related to the change in the C—H bond order[17] as well as to its length.[18] Hence, one can assume that the orientational sensitivity of the direct spin-spin coupling constant ^{13}C—^{1}H is greater than that of the proton chemical shift, which causes a more pronounced increase in the spin-spin coupling constant ^{13}C—^{1}H when linear intermolecular hydrogen bonds are formed than when nonlinear intramolecular hydrogen bonds are formed.

References

1. O. A. Reutov, I. P. Beletskaya, and K. P. Butin, *CH-kisloty* [*CH-Acids*], Nauka, Moscow, 1980, 247 pp. (in Russian).
2. V. K. Pogorelyi and T. B. Vishnyakova, *Usp. Khim.*, 1984, **53**, 1985 [*Russ. Chem. Rev.*, 1984, **53** (Engl. Transl.)].
3. R. L. Lichter and J. D. Roberts, *J. Phys. Chem.*, 1970, **74**, 912.
4. T. Gramstad and O. Mundheim, *Spectrochim. Acta*, 1972, **28A**, 1405.
5. D. F. Evans, *J. Chem. Soc.*, 1963, 5575.
6. M. P. Sammes, R. L. Harlow, and S. H. Simonsen, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1126.
7. A. V. Afonin and M. A. Andriyankov, *Zh. Org. Khim.*, 1988, **24**, 1034 [*J. Org. Chem. USSR*, 1988, **24** (Engl. Transl.)].
8. M. P. Sammes and R. L. Harlow, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1130.
9. A. V. Afonin, M. V. Sigalov, S. E. Korostova, I. A. Aliev, A. V. Vashchenko, and B. A. Trofimov, *Magn. Reson. Chem.*, 1990, **28**, 580.
10. A. V. Afonin, A. V. Vashchenko, M. A. Andriyankov, V. K. Voronov, E. I. Enikeeva, and L. L. Dmitrieva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1539 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1392 (Engl. Transl.)].
11. A. V. Afonin, E. S. Domnina, L. V. Baikalova, and V. K. Voronov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2747 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2489 (Engl. Transl.)].
12. A. V. Afonin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1344 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1185 (Engl. Transl.)].
13. A. V. Afonin, A. V. Vashchenko, V. K. Voronov, B. V. Trzhtsinskaya, N. D. Abramova, and Z. V. Stepanova, *Zh. Org. Khim.*, 1990, **26**, 411 [*J. Org. Chem. USSR*, 1990, **26** (Engl. Transl.)].
14. A. V. Afonin, B. A. Trofimov, S. F. Malysheva, and A. V. Vashchenko, *Zh. Org. Khim.*, 1992, **28**, 225 [*J. Org. Chem. USSR*, 1992, **28** (Engl. Transl.)].
15. L. C. Allen, *J. Am. Chem. Soc.*, 1975, **97**, 6921.
16. H. Guenther, *NMR Spectroscopy: An Introduction*, J. Wiley & Sons, Chichester, 1980, 436 pp.
17. A. V. Afonin, A. V. Vashchenko, and D. K. Danovich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 582 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 503 (Engl. Transl.)].
18. C. Vizioli, M. C. Ruiz de Azua, C. G. Giribet, R. H. Contreras, L. Turi, J. J. Dannenberg, I. D. Rae, J. A. Weigold, M. Malagoli, R. Zanasi, and P. Lazzeretti, *J. Phys. Chem.*, 1994, **98**, 8858.

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