Analysis of effect of specific C—H...X interaction on the direct $^{13}C—^{1}H$ spin-spin coupling constants based on *ab initio* quantum-chemical calculations

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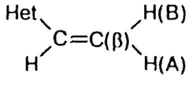
An *ab initio* quantum-chemical calculation of the direct $^{13}C—^{1}H$ spin-spin coupling constants in the $CH_4—H_2O$ system was carried out and experimental data obtained for a series of *N*-vinyl compounds were analyzed. The specific C—H...X (X = O, N) intramolecular interactions result in increasing the direct $^{13}C—^{1}H$ spin-spin coupling constant of the hydrogen involved in bonding and decreasing the direct $^{13}C—^{1}H$ spin-spin coupling constant for the hydrogen atom that takes no part in the interaction.

Key words: *ab initio* quantum-chemical calculations; direct spin-spin coupling constants $^{13}C—^{1}H$; specific intramolecular C—H...X interactions.

Previously, exemplified by a series of vinyl compounds, the specific intramolecular C—H...X interactions of a weak hydrogen bond type were shown to result in an essential increase in the direct $^{13}C—^{1}H$ spin-spin coupling constant (SSCC) for the hydrogen atom participating in the bonding.[1–3] The principal problem in revealing the effect is its masking by $^{13}C—^{1}H$ SSCC changes caused by the electronic properties of versatile substituents at the vinyl group. The effect of specific intramolecular C—H...X interactions on the direct $^{13}C—^{1}H$ SSCC is most obvious when comparing the latter with that for the same carbon atom if one of its bonded H atoms participates in the interaction.

Two direct $^{13}C—^{1}H$ SSCC for the C(β) atom of the vinyl group ($^{1}J_{C(\beta),H(A)}$ and $^{1}J_{C(\beta),H(B)}$) in *N*-vinyl derivatives of heterocycles change uniformly with variation of the electron effect of the substituent, *i.e.*, their difference $\Delta J = {}^{1}J_{C(\beta),H(A)} - {}^{1}J_{C(\beta),H(B)}$ remains constant[4] (Scheme 1).

Scheme 1



The participation of the H(B) atom in the specific intramolecular C—H...X interaction with any endo- or exocyclic heteroatom results in drastic changes in the parameter ΔJ depending on the intramolecular distance hydrogen atom—heteroatom.[3]

This conclusion is based on comparison of experimentally measured values of the $^{13}C—^{1}H$ SSCC with the geometric characteristics of molecules obtained from the quantum-chemical calculations; no calculations of the direct $^{13}C—^{1}H$ SSCC were carried out in this case. Additionally, quantum-chemical calculations of the direct $^{13}C—^{1}H$ SSCC performed recently with consideration for the spatial effect of the unshared electron pairs of the fluorine atom indicate the sensitivity of all C—H(5) bonds to changes in the direct $^{13}C—^{1}H$ SSCC. Having regard for this, we carried out an additional analysis of changes in the direct $^{13}C—^{1}H$ SSCC in several *N*-vinyl compounds using data of *ab initio* quantum-chemical calculations of the spin-spin coupling constants of the type under study.

The calculation of the spin-spin coupling constant for the ethylene molecule is complicated by the instability of non-singlet states of unsaturated compounds in *ab initio* calculations.[6] Therefore the simplest $CH_4—H_2O$ complex was chosen as a system which allows one to simulate the effect of specific intramolecular C—H...X interaction on the direct $^{13}C—^{1}H$ SSCC at variations of the H...X (*r*) interatomic distance.

Experimental

The values of the direct $^{13}C—^{1}H$ SSCC in the $CH_4—H_2O$ system were calculated for various distances H...O using the SYSMO program[7–9] using the equations of motion method (EOM)[10] in the random phase approximation (RPA).[11] The calculations were performed in the (9s5p/5s/10s4p) basis set, which was adjusted to the [4s2p/2s/3s2p] contraction.[12]

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Table 1. Calculated values of direct $^{13}C—^{1}H$ spin-spin coupling constants in the $CH_4—H_2O$ system

r(O...H)/Å	SSCC, J/Hz			
	$^1J_{C,H(1)}$	$^1J_{C,H(2)}$	$^1J_{C,H(3)}$	ΔJ
1.65	164.68	146.75	145.91	−17.93
1.92	164.26	148.51	148.59	−15.75
2.18	162.89	150.79	150.85	−12.10
2.71	160.35	153.24	153.27	−7.11
3.77	157.84	154.80	154.81	−3.04

Note. Notations correspond to those in Scheme 2 in the text; $^1J_{C,H(3)}$ and $^1J_{C,H(4)}$ are equivalent.

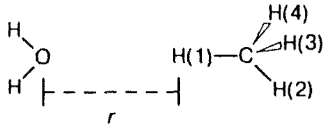
The geometry optimized in the 6-31 G basis set and the standard one[13] were used in calculations of the water molecule and of the $^{13}C—^{1}H$ SSCC of the CH_4 molecule, respectively. No additional optimization of geometry was performed as the intermolecular distance H...O in the $CH_4—H_2O$ system was varied since the expected interval of changes in the bond lengths was less than 0.01 Å[5,14] and the corresponding changes in $^{13}C—^{1}H$ SSCC were no larger than 1 Hz.[15] The geometry of *N*-vinyl compounds was optimized by the AM1 method.[16]

The proton-coupled ^{13}C NMR spectra of compounds under study were recorded on Tesla BS 567 A and Bruker WP 200 SY spectrometers (51.1 and 50.3 MHz, respectively) in $CDCl_3$. The assignment of the direct $^{13}C—^{1}H$ SSCC for the C(β) atom of the vinyl group was performed by satellite signals in ^1H NMR spectra. Spectral simulations were carried out on an Aspect-2000 minicomputer using the standard PANIC program. The accuracy of measurements of the $^{13}C—^{1}H$ SSCC was ±0.1 Hz.

Results and Discussion

The calculated values of the $^{13}C—^{1}H$ SSCC for five intermolecular distances r are represented in Table 1 in accordance with the notations in Scheme 2.

Scheme 2



The absolute values of the calculated $^{13}C—^{1}H$ SSCC exceed the real values; it is characteristic of calculations of the spin-spin coupling constants of such a type in methane.[9] It follows from the data of Table 1 that the spin-spin coupling constant $^1J_{C,H(1)}$ is considerably increased with decreasing r-distance, while the opposite tendency is observed for the other three spin-spin coupling constants ($^1J_{C,H(2)}$, $^1J_{C,H(3)} = {}^1J_{C,H(4)}$).

The dependence of the above mentioned SSCC on the distance r qualitatively corresponds to that one in complex $CH_4—HF$,[5] but is somewhat steeper. The difference between the values of the SSCC of the noninteracting hydrogen atom and that involving in the interaction (the ΔJ parameter) serves as an experimental criterion of the specific intramolecular C—H...X interaction. Because of this, the dependence $\Delta J = {}^1J_{C,H(2)} - {}^1J_{C,H(1)}$ on the distance r in complex $CH_4—H_2O$ was examined (Fig. 1).

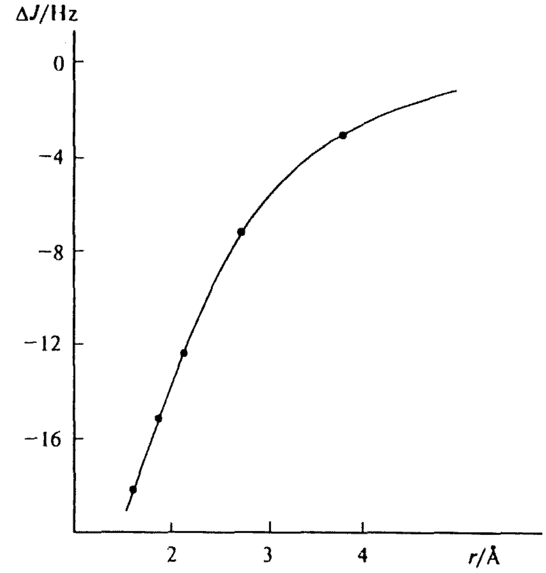


Fig. 1. Dependence of ΔJ on the H—O bond length in the $CH_4—H_2O$ complex.

It was shown previously[17] that an analogous dependence of the shielding constants on the intermolecular distance is well interpolated by polynomials of degrees in r. In this case, the dependence $\Delta J(r)$ is described by a simple equation:

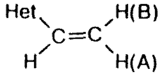
$$\Delta J = 8.9 - 45.3r^{-1};\ r = 0.99. \quad (1)$$

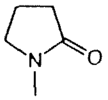
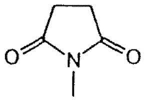
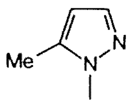
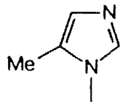
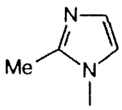
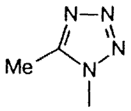
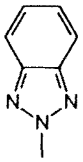
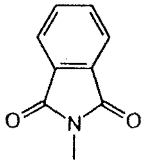
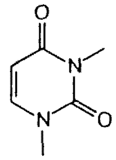
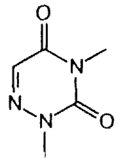
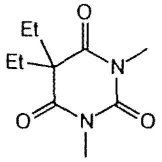
Thus, in the $CH_4—H_2O$ complex, changes in the ΔJ parameter are inversely proportional to the distance r.

The experimental values of the $^{13}C—^{1}H$ SSCC of the C(β) atom of the vinyl group for a number of *N*-vinyl derivatives of heterocycles (**1—12**) are listed in Table 2. The equilibrium distances between the H(B) hydrogen atom and the nearest endo- or exocyclic heteroatom r(X...H(B)) calculated by AM1 method are also given in Table 2.

As the H(B) atom and the heteroatom come closer a pronounced increase in the $^1J_{C(\beta),H(B)}$ SSCC is observed. Thus, in molecules **1**, **4**, **5**, **7**, and **10a** where r(X...H(B)) lies in the range from 4.20 to 4.93 Å, the $^1J_{C(\beta),H(B)}$ SSCC is changed from 156.1 to 158.5 Hz. With decreasing distance r(X...H(B)) to 2.71—2.83 Å in compounds **3**, **6**, **8**, and **11a**, the $^1J_{C(\beta),H(B)}$ SSCC is increased to 161.3—162.7 Hz. With a further decrease in the distance r(X...H(B)) to 2.24—2.34 Å in the derivatives **2**, **9**, **10b**, **11b**, and **12** the $^1J_{C(\beta),H(B)}$ SSCC continues increase to 163.1—165.3 Hz.

Table 2. Experimental values of direct $^{13}C-^{1}H$ spin-spin coupling constants and calculated r(X...H(B)) bond lengths for *N*-vinyl derivatives of heterocycles **1—12**



Compound	Het	r(X...H(B)) /Å	SSCC, J/Hz		
			$^1J_{C(\beta),H(A)}$	$^1J_{C(\beta),H(B)}$	ΔJ
1		4.93	163.1	156.1	7.0
2		2.32	160.7	163.1	−2.4
3		2.79	162.9	161.3	1.6
4		4.20	164.4	157.7	6.7
5		4.91	164.5	157.5	7.0
6		2.83	165.7	162.7	3.0
7		4.24	165.2	158.5	6.7
8		2.73	164.7	162.0	2.7
9		2.34	160.9	163.7	−2.8
10a		4.82	165.5	157.2	8.3
10b		2.24	159.5	164.3	−4.8
11a		2.71	163.3	162.1	1.2
11b		2.25	160.0	165.3	−5.3
12		2.27	160.3	163.6	−3.3

Note: **a** and **b** refer to the 1-vinyl and 3-vinyl group of compounds **10** and **11**, respectively.

At the same time, one can note a considerable decrease in the $^1J_{C(\beta),H(A)}$ SSCC in the molecules **2**, **9**, **10b**, **11b**, and **12** (159.5—160.7 Hz, see Table 2) in comparison with those of derivatives **1**, **4**, **5**, **7**, **10a** and **3**, **6**, **8**, and **11a** (162.9—165.7 Hz). The absence of any decrease in the $^1J_{C(\beta),H(A)}$ SSCC in the latter group of compounds as compared with those of compounds **1**, **4**, **5**, **7**, and **10a** is likely to be associated with the effect of heterocyclic substituents of greater electron-acceptor ability, which causes an increase in the constants for the first group of molecules.

The effect of the specific intramolecular C—H...X interactions on the spin-spin coupling constants $^1J_{C(\beta),H(A)}$ and $^1J_{C(\beta),H(B)}$ in compounds **1—12** is more clearly reflected in the change in the parameter $\Delta J = {}^1J_{C(\beta),H(A)} - {}^1J_{C(\beta),H(B)}$, which does not depend on the electronic effect of the heterocyclic substituents. The dependence of ΔJ on the intramolecular distance r(X...H(B)) shown in Fig. 2 is described by a polynomial of the 4th degree in r:

$$\Delta J = 10.4 - 20.4r^{-1} + 55.3r^{-2} - 96.4r^{-3} - 207.6r^{-4}; \quad r = 0.99. \qquad (2)$$

It is obvious that the dependence of the empirical ΔJ parameter on the distance r is more complicated than the theoretical relationship (1). It may be due to several factors.

Firstly, compounds **1—12** differ in their equilibrium values of the torsion angle φ, which is characteristic of the hindered rotation of the vinyl group (see Table 2). The torsion angle φ in the molecules **1—10a** and **11a** remains virtually constant (φ = 0—1°), but it is increased considerably in the derivatives **10b**, **11b**, and **12**

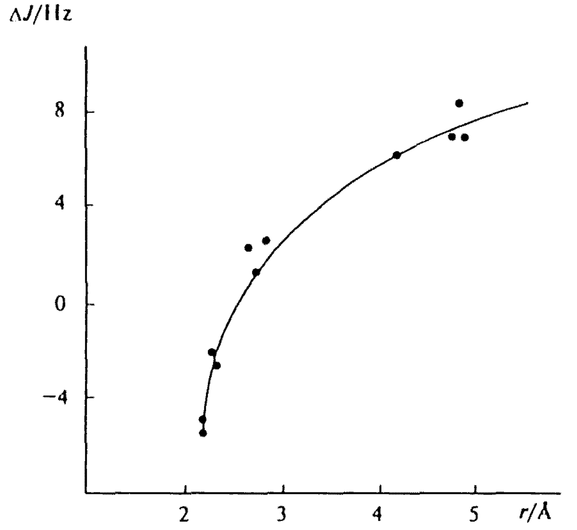


Fig. 2. Dependence of ΔJ on the H...O(N) bond length in compounds **1**—**12**.

(φ = 17—23°). Secondly, slight changes in the bond angles and bond lengths, which provide a spread of ΔJ values, occur in various *N*-vinyl compounds. Thirdly, the interaction C—H...O is realized in the molecules **2**, **9**, **10b**, **11b**, and **12** whereas the C—H...N interaction occurs in the derivatives **3**, **6**, **8**, **11b**. The latter seems to be insignificant since the ^{13}C—^{1}H SSCC in the systems CH_4—HF and CH_4—H_2O with equal hydrogen atom—heteroatom distances (*i.e.*, with O atom in place of F atom) differ slightly (see this work and Ref. 5).

At the same time, both the empirical (2) and theoretical (1) dependences exhibit a qualitative similarity. The main difference consists in a sharper decrease in the ΔJ parameter with decreasing distance r in the *N*-vinyl compounds than that in the CH_4—H_2O complex (see Figs. 1 and 2). This is mainly due to the much more acid character of the C—H bond in the *N*-vinyl group than that in methane.[18] In addition, the bicoordinated oxygen atom has a lesser ability to form hydrogen C—H...X bonds than a monocoordinated oxygen atom and bicoordinated nitrogen atom.[19]

Thus, the *ab initio* calculations of the direct ^{13}C—^{1}H SSCC in the CH_4—H_2O system as well as the analysis of their experimental values indicate that the specific intramolecular C—H...X interaction causes two interrelated spectral effects. Firstly, an increase in the direct ^{13}C—^{1}H SSCC of the hydrogen atom participating in the interaction is observed. Secondly, a considerable decrease in the direct ^{13}C—^{1}H SSCC of the hydrogen atom not involved in the specific bonding takes place. The latter was not pointed out previously.[1—3] The selective character of changes in the direct ^{13}C—^{1}H SSCC in the formation of the specific intramolecular C—H...X interactions offers new possibilities for studying the stereochemistry of the processes of interaction between CH-acids and organic bases.

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