Dependence of geminal $^1H—^1H$ and $^{31}P—^1H$ spin-spin coupling constants on the specific intramolecular C—H...X interaction

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Participation of the proton in a specific intramolecular C—H...X (X = N, O) interaction leads to an increase in its geminal $^1H—^1H$ and $^1H—^{31}P$ spin-spin coupling constants (SSCC). According to *ab initio* calculations carried out in the 6-31G** basis set, the observed effect is mainly due to the change in the diamagnetic spin-orbital contribution to SSCC.

Key words: specific intramolecular C—H...X interactions, geminal $^1H—^1H$ and $^{31}P—^1H$ spin-spin coupling constants, *ab initio* calculations; diamagnetic spin-orbital interaction.

Previously,[1—5] we have established that the specific intramolecular C—H...X (X = N, O, S) interactions of a weak H-bond type essentially affect the NMR spectral parameters. In this case, the signals of both ^{13}C [1] and the heteroatom[3] involved in the interaction are shifted upfield, and an increase in the corresponding direct $^{13}C—^1H$ spin-spin coupling constant (SSCC)[1,2,4] and the geminal $^1H—^1H$ SSCC of the protons (one of which is involved in the C—H...X interaction) occurs.[2,4,5] However, the nature and the mechanism of this phenomenon have not been studied yet.

Heterocyclic *N*-vinyl derivatives are convenient model subjects for experimental studies of the dependence of geminal SSCC on specific intramolecular C—H...X interactions. The participation of the β-*cis*-proton of the vinyl group in a C—H...X interaction with an endo- or exocyclic heteroatom leads to an increase in the geminal $^1H—^1H$ SSCC.[2,4,5] In the present work, a large series of compounds of this kind was studied, and the specific intramolecular C—H...X interactions were found to affect the geminal $^1H—^{31}P$ SSCC.

To elucidate the mechanism of the effects, *ab initio* calculations of geminal $^1H—^1H$ SSCC were carried out. The influence of the specific intramolecular C—H...X interactions on the geminal SSCC was simulated by modeling the spectral effects using the simplest systems.[6,7] The dependence of geminal $^1H—^1H$ SSCC on the interatomic H...X distance was studied using the supermolecule $CH_4—HF$. The use of ethylene itself in this system is complicated due to the instability of nonsinglet states of unsaturated molecules in *ab initio* calculations.[8]

Experimental

The geminal $^1H—^1H$ SSCC in the $CH_4—HF$ system were calculated using the Galasso program[9] in the 6-31G** basis set.

^1H NMR spectra were recorded on Tesla BS-567A and Bruker WP-200 SY spectrometers (100 and 200 MHz, respectively) in $CDCl_3$, with HMDS as the internal standard. When the geminal $^1H—^1H$ SSCC did not exceed 0.5 Hz, the samples were evacuated. The signs of SSCC were determined by the homonuclear INDOR method, and the results were compared with the known data.[10]

Results and Discussion

Experimental values of $^1H—^1H$ and $^{31}P—^1H$ SSCC of the vinyl group for a number of *N*-vinyl derivatives of heterocycles (1—12) are presented in Table 1. Both vinyl groups in 2,4-divinyl-1,2,4-triazol-3-one (1) are *trans*-oriented with respect to the carbonyl group[2] (Scheme 1, A).

The H_B proton of the 2-vinyl group is involved in a specific intramolecular C—H...N interaction with the nitrogen N(1) atom. Therefore, its signal is shifted downfield as compared with that of the H_B proton of the 4-vinyl group, whereas the signal of the H_A proton is shifted upfield (see Table 1: 0.1 and 0.2 ppm, respectively).[2] The participation of the H_B proton of the

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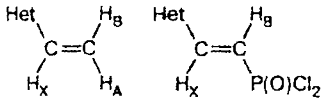
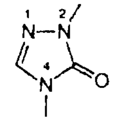
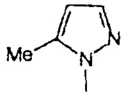
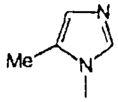
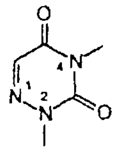
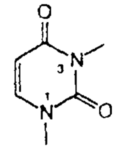
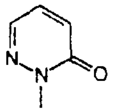
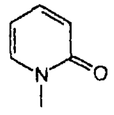
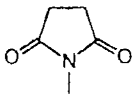
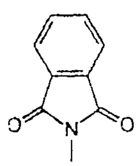
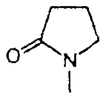
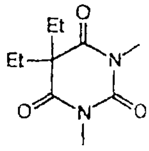
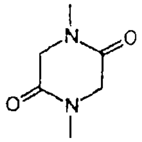
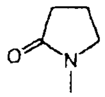
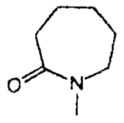
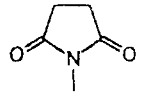
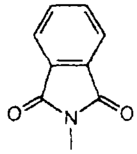
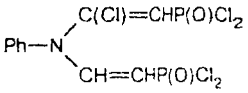
Table 1. Parameters of ^1H NMR spectra of *N*-vinyl compounds **1**—**12** and β-aminovinylphosphonic chlorides **13**—**17**



1—12 **13—17**

Compound	Het		δ		J/Hz	
			H_A	H_B	$-{}^2J_{H_A,H_B}$	$^2J_{P,H_B}$
1		4[a] 2	4.95 4.77	5.36 5.46	1.7 0.4	— —
2			4.75	5.60	0.3	—
3			4.95	5.30	1.3	—
4		2 4	4.92 5.42	5.55 6.15	0.9 0.5	— —
5		1 3	5.00 5.31	5.11 5.92	2.2 0	— —
6			4.84	5.60	0.3	—
7			5.03	5.24	1.7	—
8			5.08	6.09	0	—
9			5.04	6.07	0	—
10			4.41	4.35	0.6	—
11			5.29	5.71	0.4	—
12			4.61	4.54	1.8	—
13[b]			—	5.30	—	26.9
14[b]			—	5.41	—	26.5
15[b]			—	7.31	—	30.5
16[b]			—	7.12	—	30.1
17[b]	 $PhN(C(Cl)=CHP(O)Cl_2)(CH=CHP(O)Cl_2)$		—	—	—	18.0[c] 25.0

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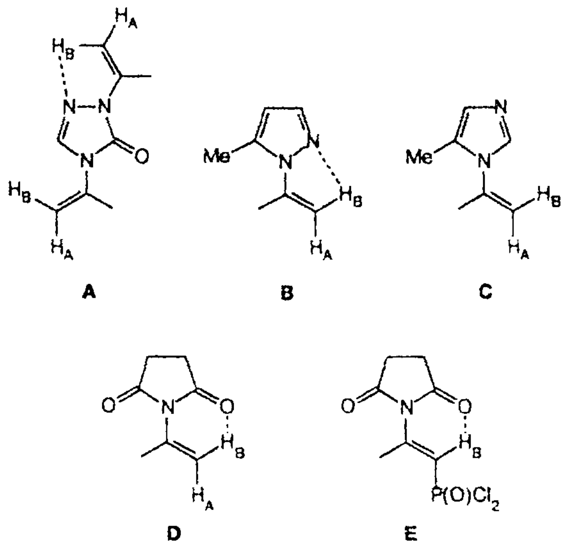
[a] The number denotes the position of the vinyl group. [b] Data from Refs. 16, 17. [c] The value for the $C(Cl)=CHP(O)Cl_2$ group.

2-vinyl group in the specific intramolecular C—H...N interaction manifests itself in the increase in the geminal $^2J_{H_A,H_B}$ SSCC of this vinyl group by 1.3 Hz as compared with that of the 4-vinyl group (see Table 1).

Scheme 1



The influence of the specific intramolecular C—H...N interaction on the geminal $^2J_{\mathrm{H_A,H_B}}$ SSCC can be illustrated if the three pairs of compounds are compared. The vinyl groups in 1-vinyl-5-methylpyrazole (**2**) and 1-vinyl-5-methylimidazole (**3**) are *trans*-oriented relative to the Me group (see Scheme 1, **B** and **C**). The H_B proton of the vinyl group of pyrazole **2** is involved in the specific intramolecular C—H...N interaction.[11] Accordingly, the signal of H_B proton in pyrazole **2** shifts downfield (by 0.3 ppm) while that of H_A proton shifts upfield (by 0.2 ppm), and the $^2J_{\mathrm{H_A,H_B}}$ SSCC increases by 1 Hz as compared with that of imidazole **3**. The vinyl groups at N(2)(N(1)) in 2,4-divinyl-1,2,4-triazine-3,5-dione (**4**), 1-vinyl-6-pyridazone (**6**), 1,3-divinyluracil (**5**), and 1-vinyl-2-pyridone (**7**) have the *s-trans*(*O*)-conformation, which ensures the specific intramolecular C—H...N interaction with participation of the H_B proton in the first two compounds.[4] The signals of H_A and H_B protons of the 2-vinyl group and those of the 1-vinyl group of compounds **4** and **6** are shifted accordingly, and $^2J_{\mathrm{H_A,H_B}}$ SSCC increase by 1.3—1.4 Hz as compared with those of compounds **5** and **7** (see Table 1).

The $^2J_{\mathrm{H_A,H_B}}$ SSCC are similarly affected by the specific intramolecular C—H...O interaction. *N*-Vinylimides (**8**, **9**) are planar, and the H_B proton interacts with the O atom of the carbonyl group[2] (see Scheme 1, **D**). In spite of the electron-withdrawing effect of the second carbonyl group (which must lead to a decrease in the geminal SSCC),[12,13] the $^2J_{\mathrm{H_A,H_B}}$ SSCC in compounds **8** and **9** increase by 0.6 Hz as compared with that in *N*-vinylpyrrolidone **10**.

Because of the specific intramolecular C—H...O interaction, the $^2J_{\mathrm{H_A,H_B}}$ SSCC of the 3-vinyl group in uracil **5** is ~2 Hz larger than that of the 1-vinyl group. Finally, an appreciable increase in the $^2J_{\mathrm{H_A,H_B}}$ SSCC is observed in molecule **11** as compared with that of piperazinedione **12** (by 1.4 Hz, see Table 1), which is also due to the specific intramolecular C—H...O interaction.[4]

Geminal ^{31}P—^{1}H SSCC are also affected by the specific intramolecular C—H...O interaction. A strong upfield shift of the signals of the H_B proton (~2 ppm, see Table 1) is observed in β-aminovinylphosphonic acid derivatives **13** and **14** as compared with those of related compounds (**15**, **16**), which is explained by the specific intramolecular C—H...O interaction (see Scheme 1, **E**). For imides **15** and **16** the geminal $^2J_{\mathrm{P,H_B}}$ SSCC is appreciably larger (by 4 Hz) than those of lactams **13**, **14**, while the electron-withdrawing effect of the second CO group had to decrease this SSCC. Thus, the $^2J_{\mathrm{P,H_B}}$ SSCC of the C(Cl)=CHP(O)Cl$_2$ fragment in compound **17** is 7 Hz smaller than that of the CH=CHP(O)Cl$_2$ fragment due to the electron-withdrawing effect of the chlorine atom (see Table 1). Hence, the influence of the specific intramolecular C—H$_B$...O interaction on the $^2J_{\mathrm{P,H_B}}$ SSCC surpasses the electron-withdrawing effect of the second CO group in compounds **15** and **16**.

Thus, the experimental data are evidence that the specific intramolecular C—H...X interaction (X is an atom with the lone electron pairs) result in an appreciable increase in the geminal ^{1}H—^{1}H and ^{31}P—^{1}H SSCC with participation of the proton involved in the interaction.

The calculated values of geminal ^{1}H—^{1}H SSCC for eight different intermolecular distances *r* are listed in Table 2. The calculations were carried out for the CH$_4$ and HF molecules arranged as shown in Scheme 2 (**F**). It is accepted that the Fermi-contact contribution (J^{FC}) is the main contribution to the ^{1}H—^{1}H SSCC.[14] Actually, this contribution to the geminal $^2J_{\mathrm{H,H}}$ SSCC ap-

Scheme 2

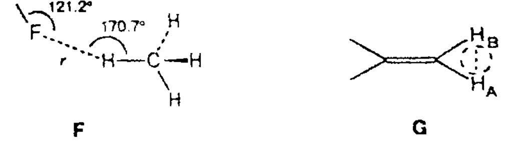


Table 2. Calculated values of the contributions to the ^{1}H—^{1}H SSCC in the CH$_4$—HF system

r (F...H) /Å	$^2J_{\mathrm{H,H}}$/Hz				
	$-J^{\mathrm{FC}}$	$-J^{\mathrm{PSO}}$	$-J^{\mathrm{DSO}}$	$-J^{\mathrm{SD}}$	$-J^{\mathrm{tot}}$
1.6	30.20	0.96	2.47	0.24	33.87
1.8	30.21	0.97	2.65	0.24	34.07
2.0	30.22	0.97	2.79	0.24	34.22
2.2	30.24	0.98	2.88	0.23	34.33
2.4	30.26	1.00	2.94	0.23	34.43
2.6	30.30	1.00	2.99	0.23	34.52
2.8	30.35	1.01	3.02	0.23	34.61
3.0	30.40	1.02	3.05	0.23	34.70
3.2	30.45	1.02	3.07	0.23	34.77

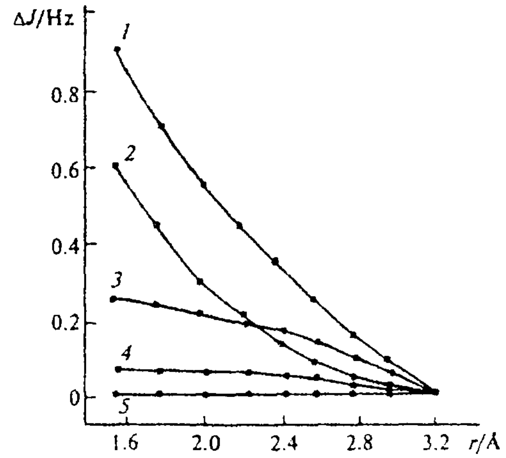


Fig. 1. Dependence of geminal $^2J_{H,H}$ SSCC and its components on the F...H distance in the CH_4—HF system: J^{tot} (*1*); J^{DSO} (*2*); J^{FC} (*3*); J^{PSO} (*4*); J^{SD} (*5*).

pears to have the largest absolute value (see Table 2). However, the Fermi-contact contribution changes only by 0.25 Hz as the intermolecular distance r(F...H) decreases from 3.2 to 1.6 Å (Fig. 1). The observed experimental trends cannot be explained by such a small change in the Fermi-contact contribution to the geminal $^2J_{H,H}$ SSCC. Consequently, this approximation is inconsistent with the spectral effect in question.

Generally, the total value of the SSCC (J^{tot}) is determined by the sum of the Fermi-contact (J^{FC}), the paramagnetic spin-orbital (J^{PSO}), the diamagnetic spin-orbital (J^{DSO}), and the spin-dipole (J^{SD}) contrubutions (Eq. (1)).[8]

$$J^{tot} = J^{FC} + J^{PSO} + J^{DSO} + J^{SD}. \tag{1}$$

The calculation of all contributions to the geminal $^2J_{H,H}$ SSCC in the CH_4—HF system (see Table 2) showed that the diamagnetic spin-orbital contribution to the SSCC is highly sensitive to the intermolecular distance r (see Fig. 1). The value of J^{DSO} increases by 0.6 Hz as r decreases from 3.2 to 1.6 Å. Since J^{DSO} is only a contribution of the first-order perturbation, these values are small, and they are often ignored in theoretical studies.[14] However, in this case the changes in J^{DSO} appear to be the most significant. Changes in J^{PSO} are insignificant, and J^{SD} remains constant (see Fig. 1). The overall calculated change in J^{FC} and J^{DSO} (0.85 Hz) fits the experimental one well in the order of magnitude.

It is of interest to consider the physical meaning of the change in the J^{DSO}. For the two nuclei (N and M) interacting with each other, J^{DSO} is defined by formula (2):[15]

$$J^{DSO}_{NM} = k\sum_{i=1}^{n}\left\langle \varphi_i \left| \frac{\bar{r}_N\bar{r}_M}{(r_N r_M)^3} \right| \varphi_i \right\rangle , \tag{2}$$

where $\bar{r}_N$ and $\bar{r}_M$ are radius vectors of the i-th electron relative to the N and M nuclei, respectively, and φ_i is its wave function.

The geometric peculiarity of the operator of diamagnetic spin-orbital interaction is that its value inside the sphere of the diameter equal to the distance between the N and M nuclei is negative; however, its value is positive outside this sphere.[15] For the geminal H_A and H_B protons of the vinyl group, this means that an additional increase in the electron density outside the sphere of a H_A—H_B diameter (see Scheme 2, G) should lead to a substantial increase in the contribution of J^{DSO} to the $^2J_{H_A,H_B}$ SSCC.

It is this situation that is realized in compounds **2**, **4**, **6**, **8**, **9**, **11**, **15**, and **16**, in which specific intramolecular C—H...X interactions occur when additional electron density outside the sphere of a H_A—H_B diameter is provided by the lone electron pair of the X heteroatom.

Thus, the geminal SSCC are of significant importance as probes for detecting the areas in the molecule with higher electron density (lone electron pairs and π-systems).

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