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Study of stereochemical dependences of the direct $^{13}C-^{1}H$ spin-spin coupling constants in vinylpyridines by the quantum-chemical INDO-RPA method

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The stereochemical dependences of the direct $^{13}C-^{1}H$ spin-spin coupling constants (SSCC) in the vinyl group of vinylpyridines studied by the quantum-chemical INDO-RPA method indicate that the steric closeness of the hydrogen atom to the nitrogen atom causes an increase in the corresponding direct $^{13}C-^{1}H$ SSCC and a decrease in the analogous constant of the geminal hydrogen atom. The results obtained qualitatively agree with the data of *ab initio* calculations for the simplest systems and the experiment. At the same time, an essential quantitative overestimation of the real effect takes place.

Key words: effect of steric closeness of a heteroatom on the direct $^{13}C-^{1}H$ spin-spin coupling constants; quantum-chemical calculations, INDO-RPA method.

In our previous works,[1–5] vast experimental data on the stereoselectivity of the direct $^{13}C-^{1}H$ spin-spin coupling constant (SSCC) in the vinyl group of various vinyl compounds have been obtained. A particular kind of stereoselectivity of the direct $^{13}C-^{1}H$ SSCC found was associated with their increase in the case of steric approach of the corresponding hydrogen atom to the heteroatom.[1,3–5] 2-Vinylpyridine is one of the molecules in which this effect is clearly seen.[1]

Previously,[5] the effect of steric closeness of the heteroatom on the direct $^{13}C-^{1}H$ SSCC was studied using *ab initio* quantum-chemical calculations of the simplest intermolecular system, CH_4-H_2O. However, no calculations of such effect were carried out for more complex molecules. The aim of this work is to study the effect of steric C—H...N interaction on the direct $^{13}C-^{1}H$ SSCC in the molecule of 2-vinylpyridine by the semiempirical INDO-RPA method and to compare the results obtained with the experimental values and the data of *ab initio* calculations.

Experimental

Calculations of the direct $^{13}C-^{1}H$ SSCC were carried out by the semiempirical method of intermediate neglect of differential overlap (INDO)[6] in the random phase approximation

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Table 1. Calculated ^{13}C—^{1}H SSCC in the vinyl group of vinylpyridines depending on the distance (*r*)

Compound	SSCC, *J*/Hz			*r*(N...H$_B$)
	$^{1}J_{\mathrm{C(\beta),H_B}}$	$^{1}J_{\mathrm{C(\beta),H_A}}$	$-\Delta J$	/Å
cis(*N*)-2-Vinylpyridine* (**1**)	169.2	144.0	25.2	2.56
	166.8	146.7	20.1	2.61
	164.5	149.2	15.3	2.66
	163.1	150.8	12.3	2.69
trans(*N*)-2-Vinylpyridine (**1**)	163.3	151.3	12.0	
4-Vinylpyridine (**3**)	161.6	151.4	10.2	

* Values at the bond angle ε (see Scheme 1) of 120, 122, 124, and 125°, respectively; ε = 120° corresponds to the equilibrium geometry.

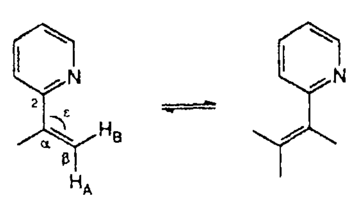
(RPA).[7] The molecular geometry was optimized by the semiempirical quantum-chemical AM1 method.[8]

The proton-coupled ^{13}C NMR spectra of vinylpyridines were recorded on a Bruker WP 200 SY spectrometer (200.3 MHz) in CDCl$_3$. The assignment of the direct ^{13}C—^{1}H SSCC for the β-carbon atom of the vinyl group was performed by satellite signals in ^{1}H 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 ^{13}C—^{1}H SSCC for the β-carbon atom of the vinyl group of 2-vinylpyridine (**1**) and those of 4-vinylpyridine (**3**) are presented in Table 1. No consideration has been given here to the values of SSCC for the α-carbon atom of the vinyl group since they exhibit no stereoselectivity.[1—4] Since compound **1** exists as a mixture of planar *s-cis*(*N*)- and *s-trans*(*N*)-conformers (Scheme 1), the ^{13}C—^{1}H SSCC were calculated for both forms. It was found that the obtained values of SSCC of the β-carbon atom of the vinyl group for the two conformations of 2-vinylpyridine (**1**) differ significantly.

Scheme 1



The $^{1}J_{\mathrm{C(\beta),H_B}}$ SSCC for the equilibrium geometry of the *s-cis*(*N*)-conformer of **1** is 6 Hz larger, and the $^{1}J_{\mathrm{C(\beta),H_A}}$ SSCC is 7 Hz smaller than those for the optimized structure of the *s-trans*(*N*)-conformer. The H$_B$ and N atoms in the *s-cis*(*N*)-conformation of compound **1** (see Scheme 1) are brought to close proximity.

Table 2. Experimental values of the ^{13}C—^{1}H SSCC in the vinyl group of vinylpyridines

Compound	SSCC, *J*/Hz		
	$^{1}J_{\mathrm{C(\beta),H_A}}$	$^{1}J_{\mathrm{C(\beta),H_B}}$	ΔJ
2-Vinylpyridine (**1**)	160.3	155.5	4.8
3-Vinyl-6-methylpyridine (**2**)	161.1	154.5	6.6
4-Vinylpyridine (**3**)	161.7	155.0	6.7

Thus, the increase in the calculated $^{1}J_{\mathrm{C(\beta),H_B}}$ SSCC in the *s-cis*(*N*)-conformer of compound **1** corresponds to the experimentally observed trend of its increase when the hydrogen atom and the heteroatom approach each other.[1,3—5] The direct ^{13}C—^{1}H SSCC for the geminal H$_A$ atom decreases simultaneously, which is also consistent with empirical regularities and the data of *ab initio* quantum-chemical calculations.[5,10] At the same time, the $^{1}J_{\mathrm{C(\beta),H_A}}$ and $^{1}J_{\mathrm{C(\beta),H_B}}$ SSCC in the *s-trans*(*N*)-conformer of compound **1** and those in vinylpyridine (**3**), where the nitrogen atom is distant from the vinyl group, differ insignificantly.

To make a quantitative estimate of the effect of steric closeness of the heteroatom on the direct ^{13}C—^{1}H SSCC in the vinyl group, their difference ($\Delta J = {}^{1}J_{\mathrm{C(\beta),H_A}} - {}^{1}J_{\mathrm{C(\beta),H_B}}$) was used since it does not depend on the electronic effect of the substituent in this group.[1—5] The calculated value of ΔJ is decreased by 13 Hz on going from the *s-trans*(*N*)- to the *s-cis*(*N*)-conformer of compound **1**, while those for the *s-trans*(*N*)-conformation of this molecule and compound **3** differ by less than 2 Hz (see Table 1).

The experimental $^{1}J_{\mathrm{C(\beta),H_A}}$ and $^{1}J_{\mathrm{C(\beta),H_B}}$ SSCC in 2-, 3-, and 4-vinylpyridines (**1—3**), presented in Table 2, differ from those calculated by the INDO-RPA method by 10—15 Hz, which is within the conventional limits of deviations in calculations of the direct ^{13}C—^{1}H SSCC.[11] Since the barrier to the internal rotation of the vinyl group in **1** is only 2—3 kcal mol^{-1},[12] the experimental values of $^{1}J_{\mathrm{C(\beta),H_A}}$ and $^{1}J_{\mathrm{C(\beta),H_B}}$ SSCC correspond to their averaged values for the *s-cis*(*N*)- and the *s-trans*(*N*)-conformers. Therefore, the effect of steric closeness of the nitrogen atom on the $^{1}J_{\mathrm{C(\beta),H_A}}$ and $^{1}J_{\mathrm{C(\beta),H_B}}$ SSCC in compound **1** manifests itself only in part.

The experimental value of the $^{1}J_{\mathrm{C(\beta),H_B}}$ SSCC in **1** is 0.5—1.0 Hz larger, and that of the $^{1}J_{\mathrm{C(\beta),H_A}}$ SSCC is 1.0—1.5 Hz smaller than those in 3- and 4-vinylpyridines (**2**, **3**). The parameter ΔJ for **1** is 2 Hz smaller than those for compounds **2** and **3** (see Table 2). Thus, there is a qualitative agreement between changes in the experimental and those in the calculated $^{1}J_{\mathrm{C(\beta),H_A}}$ and $^{1}J_{\mathrm{C(\beta),H_B}}$ SSCC in molecules **1—3**. However, the appreciable quantitative overestimation of the effect of steric closeness of the nitrogen atom on the $^{1}J_{\mathrm{C(\beta),H_A}}$ and

$^{1}J_{C(\beta),H_B}$ SSCC in calculations by the INDO-RPA method cannot be ignored, even if averaging of the SSCC discussed in the experimental measurements is taken into account.

In this connection a necessity arises to establish the limits of the use of the semiempirical INDO-RPA method when the effect of nonvalent interactions on the ^{13}C—^{1}H SSCC is studied. In Table 1, the calculated values of the $^{1}J_{C(\beta),H_A}$ and $^{1}J_{C(\beta),H_B}$ SSCC in the *s-cis*(*N*)-conformer of **1** are listed. They were obtained by varying the bond angle C(2)—C(α)—C(β) (ε, see Scheme 1), which allows one to change the interatomic N...H$_B$ distance. It can be seen from Table 1 that a successive increase in the $^{1}J_{C(\beta),H_A}$ SSCC and a decrease in the $^{1}J_{C(\beta),H_B}$ SSCC occurs as the angle ε and the N...H$_B$ distance increase. As the angle ε in the *s-cis*(*N*)-conformation of **1** varies from 120 to 125°, the value of ΔJ increases by 13 Hz and becomes nearly the same as those of the *s-trans*(*N*)-conformer of this molecule or compound **3**. Hence, increasing the N...H$_B$ distance results in a sharp decay of the effect of steric closeness of the heteroatom on the direct ^{13}C—^{1}H SSCC.

In Ref. 5 we interpolated the dependence of the parameter ΔJ on the hydrogen atom...heteroatom distance by corresponding power polynomials. Equations (1) and (2) were obtained from the nonempirical calculations of the CH_4—H_2O system and by interpolation of the experimental data for a wide range of *N*-vinyl derivatives of heterocycles, respectively:

$$\Delta J = 8.9 - 45.3\,r^{-1}, \qquad (1)$$

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

As the angle ε varies from 120 to 125°, the r values for molecule **1** vary in the interval from ~2.56 to 2.69 Å (see Table 1). Interpolation (1) and Eq. (2) predict a decrease in the difference ΔJ for such values of r (by 0.9 and 1.3 Hz, respectively). According to the INDO-RPA method, parameter ΔJ should decrease by 13 Hz (see Table 1).

A semiempirical calculation by the INDO-RPA method overestimates the effect of steric closeness of the heteroatom by an order of magnitude as compared to *ab initio* calculations and pure empirical estimates, while it adequately reproduces the direction of changes in the ^{13}C—^{1}H SSCC. The same conclusion also follows from a comparison of the experimental and the calculated ^{13}C—^{1}H SSCC in molecules **1**—**3**. It is likely that the potentialities of the semiempirical approximation are restricted by the qualitative analysis of changes in these spectral parameters due to the nonvalent intramolecular interactions.

References

1. A. V. Afonin, V. K. Voronov, and M. A. Andriyankov, *Khim. Geterotsikl. Soedin.*, 1986, 1568 [*Chem. Heterocycl. Compd.*, 1986 (Engl. Transl.)].
2. A. V. Afonin, M. V. Sigalov, V. K. Voronov, E. Yu. Shmidt, and B. A. Trofimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1418 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1311 (Engl. Transl.)].
3. A. V. Afonin, A. V. Vashchenko, D. K. Danovich, B. V. Trzhtsinskaya, L. V. Baikalova, and E. V. Apakina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1676 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1538 (Engl. Transl.)].
4. 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.)].
5. A. V. Afonin, S. Vizioli, M. Ruiz de Azua, and R. Kh. Contreras, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1362 [*Russ. Chem. Bull.*, 1996, **45**, 1292 (Engl. Transl.)].
6. J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970.
7. J. Oddershede, *Adv. Quantum. Chem.*, 1978, **11**, 275.
8. M. J. S. Dewar and J. J. P. Stewart, *AMPC, Program No. 527, Quantum Chemistry Program Exchange*, University of Indiana, Bloomington, IN, 1986.
9. V. Barone, N. Bianchi, F. Lelj, G. Abbate, and N. Russo, *J. Mol. Struct. (Theochem.)*, 1984, **108**, 35.
10. C. Vizioli, M. 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.
11. G. Fronzoni and V. Galasso, *J. Magn. Reson.*, 1987, **71**, 229.
12. C. H. Reynolds, *J. Mol. Struct. (Theochem.)*, 1988, **163**, 79.

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