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DIRECT $^{13}C-^{13}C$ SPIN-SPIN COUPLING CONSTANTS IN THE VINYL GROUP OF N-VINYLAZOLES

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The unshared electron pair of the dicoordinated nitrogen atom introduces a stereospecific contribution to the $^{13}C-^{13}C$ spin-spin coupling constant (SSCC) in the vinyl group of a series of N-vinylazoles, the value of which depends on the energetics of the unshared pair.

Studies of direct $^{13}C-^{13}C$ SSCC showed their sensitivity to electronic effects of the surroundings and also stereospecificity allowing these parameters to be used for conformation and analysis [1-4]. The electronegativity of the substituent is the basic factor determining the value of $^1J_{CC}$ in the vinyl group. In monosubstituted ethylene, this constant changes in the range 54.7-82.2 Hz, increasing with an increase in the electronegativity of the substituent [5]. The spatial proximity to the interacting carbon nuclei of an unshared electron pair (UEP) of a heteroatom (nitrogen or oxygen) can introduce an additional contribution to the $^1J_{CC}$ value [1-4]. The increase in $^1J_{CC}$ of the vinyl group in S-trans-conformers of alkylvinyl esters, reaching 4 Hz [2], serves as an example of this effect. In this work, $^1J_{CC}$ of the vinyl group in a series of N-vinylazoles (I-XIX) are determined and their relation to the electronic and spatial structure of this class of compounds is analyzed.

The $^1J_{CC}$ values in the vinyl group of N-vinylazoles (Table 1) changes in the range 76.5-79.7 Hz and the obvious tendencies in the changes in $^1J_{CC}$ upon increasing the number of nitrogen atoms in the azole ring are not followed. For example, for N-vinylpyrrole (77.5 Hz [5]) and 1-vinyl-5-methyltetrazole, XV, they coincide. More noticeable changes in $^{13}C-^{13}C$ SSCC (up to 2 Hz) are observed for the pairs of compounds IV and V, XII and XIII, upon introducing substituents in the 5 position of the azole ring. The data of [6, 7] allow the assumption to be made that such a substituent leads to a stabilization of the S-cis-conformer due to steric reasons (relative to the $N_{(2)}$ atom of N-vinylazoles (A), where the UEP of $N_{(2)}$ is in the spatial proximity to the vinyl C=C bond), while N-vinylazoles unsubstituted in the

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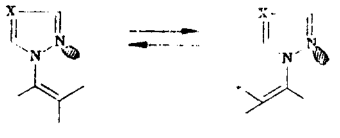
TABLE 1. Parameters of the ^{13}C NMR Spectra of the Vinyl Group of N-Vinylazoles and Calculation of the Energy of the LMO Occupied by the UEP of the $N(_2)$ Nitrogen Atom, E_n, Het$-C_\alpha H{=}C_\beta H_2$

Compound		^1J, Hz		δ C_β, ppm	E_n, eV
number	name	C_α–C_β	C_α–H		
I	1-Vinylindole	76,6	—	96,48	—
II	1-Vinyl-4,5,6,7-tetrahydroindole	77,1	—	95,52	—
III	9-Vinylcarbazole	76,5	—	101,56	—
IV	1-Vinylpyrazole	77,7	177,9	99,57	—
V	1-Vinyl-3,5-dimethylpyrazole	79,7	173,9	98,94	−20,7
VI	1-Vinylindazole	78,2	—	96,48	−20,8
VII	2-Vinylindazole	77,8	—	104,56	—
VIII	1-Vinylimidazole	76,8	178,0	101,17	—
IX	1-Vinyl-2-methylimidazole	77,3	176,5	101,12	—
X	1-Vinylbenzimidazole	77,0	—	101,57	—
XI	1-Vinyl-2-methylbenzimidazole	76,5	—	105,10	—
XII	1-Vinyl-1,2,4-triazole	77,8	181,1	103,78	—
XIII	1-Vinyl-5-methyl-1,2,4-triazole	79,0	178,5	103,58	−21,1
XIV	1-Vinylbenzotriazole	77,4	—	103,51	−22,0
XV	1-Vinyl-5-methyltetrazole	77,5	—	109,74	−22,3
XVI	1-Vinyl-5-vinyltetrazole	77,6	—	111,57	—
XVII	2-Vinyltetrazole	77,8	—	109,64	—
XVIII	2-Vinyl-5-methyltetrazole	77,8	—	107,93	—
XIX	2-Vinyl-5-vinyltetrazole	77,8	—	109,21	—

5 position exists as an equilibrium mixture of S-cis- and S-trans-conformers (A and B, respectively).



A X=CH, N B

Therefore, it can be assumed that the large $^1J_{CC}$ values in 5-substituted azoles V and XIII by comparison to their unsubstituted analogs IV and XII are related to the additional positive contribution of the UEP to the ^{13}C—^{13}C SSCC. This rule of change in $^1J_{CC}$ is related to the effect of the UEP on a pyridine-type nitrogen atom since from analysis of increments in the ^{13}C—^{13}C SSCC for the CH_3 group in similar systems [8, 9] it follows that introduction of a methyl group in the 5 position of a pyrazole or triazole ring should not lead to a noticeable change in $^1J_{CC}$. An analogous effect, related to the UEP of an sp^2-hybridized nitrogen atom was noted in [1].

The effect of the pyridine-type UEP of the nitrogen atom on the $^1J_{CC}$ SSCC is also followed in a series of N-vinylazoles with condensed and six-membered rings I-III, VI, X, XI, and XIV. Thus, in compounds I-III, X, and XI there is no such atom in the vicinity of the vinyl group and the $^1J_{CC}$ value lies in the narrow range from 76.5 to 77.1 Hz. However, for 1-vinylindazole (VI) which has the UEP of the pyridine-type nitrogen atom and the vinyl C=C bond in spatial proximity as a result of the S-cis-conformation, $^1J_{CC}$ increases to 78.2 Hz. In addition, the increase in $^1J_{CC}$ of 1-vinylbenzotriazole (XIV), similar in structure to indazole VI, is insignificant (77.4 Hz); a fact which will be discussed below.

The N-vinylazoles I-XIII can be divided into three groups based on the position of the observed effect of the UEP of the pyridine-type nitrogen atom on the $^1J_{CC}$ SSCC through space.

The first contains azoles I-III and VIII-XI, in which the effect is absent. For example, in 1-vinylimidazole (VIII) the UEP of the pyridine-type nitrogen atom is spatially removed from the vinyl group in every conformation and this agrees with the insignificant difference in $^1J_{CC}$ in compound VIII and its 2-methylsubstituted partner IX.

Vinylazoles IV, VII, and XII which are unsubstituted in the 5 position and have a pyridine-type nitrogen atom in the 2 position are placed in the second group. In these compounds the effect is not exhibited completely because of the existence of the S-transform in which the UEP of $N(_2)$ and the vinyl group are spatially separated. The $^1J_{CC}$ value in these compounds increases to 77.7-77.8 Hz.

Finally, the 5-substituted vinylazoles V, VI, and XIII with a stabilized S-cis-orientation of the vinyl group, with maximum sensitivity to the discussed effect, form the third group, whose $^1J_{CC}$ value reaches 78.2-79.7 Hz.

The N-vinyltetrazoles XV-XIX should be placed into a special group. It can be assumed that in XV and XVI, which have a substituent in the 5 position of the ring, the vinyl group is found primarily is the S-cis-orientation, and for the 2-vinyltetrazoles XVII-XIX, the proximity of the $C_\alpha{=}C_\beta$ bond to the UEP of the pyridine-type nitrogen atom is assured for any planar conformation. Therefore for all these compounds, a marked increase in the $^1J_{CC}$ value of the vinyl group should be expected. However, the $^1J_{CC}$ values of N-vinyltetrazoles XV-XIX fall in the 77.5-77.8 Hz range, characteristic of N-vinyltetrazoles of the second group.

The diminished effect of the UEP of $N(_2)$ on $^1J_{CC}$ SSCC in 1-vinylbenzotriazole XIV and N-vinyltetrazoles XV-XIX by comparison with 1-vinylindazole (VI) and 1-vinylazoles V and XIII can be related to the differences in the energetics of the UEP of the heteroatoms of the compounds discussed as has been found for $^1J_{CH}$ SSCC [10]. For a quantum chemical description of the UEP of the heteroatom, it is convenient to use the localized molecular orbital (LMO) formalism [11] within which the UEP occupies a concentric LMO which has a definite energy [12]. Table 1 gives the energies of the LMO (E_n) calculated using MNDO for the corresponding UEP of $N(_2)$ in compounds V, VI, and XIII-XV. Comparison of the E_n values and $^1J_{CC}$ for the N-vinylazoles V, VI, and XIII-XV shows the following tendency: upon lowering E_n, $^1J_{CC}$ SSCC decreases. This dependence is clearly followed in a series of N-vinyl-5-methylazoles V, XIII, and XV, where successive decrease of E_n is accompanied by successive decreases in $^1J_{CC}$ SSCC. For 1-vinylbenzotriazole (XIV), a lowering of E_n by 1.2 eV relative to 1-vinylindazole (VI) also leads to a decrease in $^1J_{CC}$ by 0.8 Hz (Table 1). The assumption can be made that as the energy of the LMO occupied by the UEP decreases the positive contribution of the UEP to $^1J_{CC}$ SSCC through space decreases.

Negative changes in the direct $^{13}C{-}^1H$ SSCC of the α-carbon of the vinyl group, $^1J_{C\alpha H}$ (Table 1)*, accompany the change of $^1J_{CC}$ SSCC in compounds IV and XII relative to the azoles V and XIII. This correlation is explained by the increase of the positive contribution of UEP to the value of $^1J_{CC}$ upon shifting the conformational equilibrium to the side of the S-cis-form leading to a lowering of this contribution to the $^1J_{C\alpha H}$ constant, and conversely, that this is important in a series of vinyl esters [2]. The $^1J_{C\alpha H}$ value can partially change due to electronic and steric effects of the substituent in the ring. However, comparison of the $^1J_{C\alpha H}$ values for N-vinylimidazole (VIII) and N-vinyl-2-methylimidazole (IX), and also analysis of $^1J_{CH}$ SSCC for 2,3-dialkylsubstituted N-vinylpyrrole [14] show that the indicated effect does not exceed 1.5 Hz. This is significantly smaller than the range of variation of $^1J_{C\alpha H}$ SSCC for compounds IV and XII, and V and XIII.

The planar conformations of N-vinylazoles (S-cis- and S-trans-) examined above are not possible for all the studied compounds. In 2,5-disubstituted N-vinylazoles, to which 9-vinylcarbazole (III) and 1-vinyl-2-methylbenzimidazole (XI) belong, the substituents in the ring are sterically prevented from being coplanar with the vinyl group and the heterocyclic fragment [15]. Therefore, the indicated compounds exist primarily in the gauche-form. A shift of equilibrium to the gauche-conformation is accompanied by a weakening of the p–π-conjugation to the vinyl group, which is consistent with the weak field shift of the C_β signal of compounds III and XI relative to their monosubstituted analogs I and X (3-5 ppm, Table 1). However, the $^1J_{CC}$ constant practically does not change upon going from compounds I and X to III and XI. Consequently, the $^1J_{CC}$ SSCC value is insensitive to perturbation of the coplanarity of the vinyl group and heterocycle and depends little on the intensity of the p–π-conjugation in the vinyl group. The $^{13}C{-}^{13}C$ SSCC of the vinyl group can be used for studying the electronic properties of the nitrogen-containing heterocycle fragments in conformationally dissimilar vinyl derivatives.

The results of this work indicate that a significant stereospecific contribution to the $^{13}C{-}^{13}C$ SSCC in the vinyl group is introduced by the UEP of the pyridine-type nitrogen atom in N-vinylazoles, i.e., between the carbon atoms located in the β- and γ-positions relative to the heteroatom. Thus, the effect of the UEP of the heteroatoms on the $^1J_{CC}$ SSCC has a general character and is found for more distant bonds between carbon nuclei, as was known

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*Only in compounds which have a single heterocycle should $^1J_{C\alpha H}$ SSCC be compared since the value of $^1J_{C\alpha H}$, in contrast to $^1J_{CC}$, is sensitive to the nature of the heterocycle [7, 14].

earlier [1-4], which expands the possibilities of using the $^1J_{CC}$ parameter for study of the stereochemistry of heteroatomic compounds, in particular for conformational analysis of nitrogen-containing heterocycles.

EXPERIMENTAL

Measurement of $^{13}C-^{13}C$ SSCC was done on a Bruker WP-200 SY spectrometer with a working frequency for ^{13}C of 50.33 MHz at a temperature of 30°C in 10 mm tubes using the impulse sequence INADEQUATE [16] in samples with naturally abundant ^{13}C. Samples were pure liquids with added acetone-D_6 (10% by volume) and 0.5-1.0% of the relaxation reagent chromium trisacetylacetonate.

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