STEREOSPECIFICITY OF DIRECT ^{13}C–^{1}H SPIN–SPIN COUPLING CONSTANTS OF VINYLPYRIDINES

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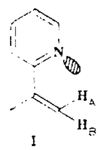
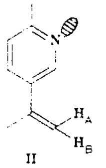
The stereospecificity of direct ^{13}C–^{1}H spin–spin coupling constants with respect to the unshared pair of a heteroatom has been widely used to study the stereochemistry of different heteroatomic and heterocyclic compounds [1]. However, the only known examples of the manifestation of this effect are ^{13}C–^{1}H spin–spin coupling constants with the participation of carbon in the α position with respect to the heteroatom.

We have established that in 2-vinylpyridine (I) the unshared pair of nitrogen introduces a significant positive contribution through the space to the ^{13}C–^{1}H spin–spin coupling constant between the cis H_A proton (with respect to the pyridine ring) and the terminal carbon of the vinyl group which is in the γ position with respect to the heteroatom. The presence of such a contribution follows from a comparison of the direct ^{13}C–^{1}H spin–spin coupling constants of the vinyl group of 2-vinylpyridine (I), 2-methyl-5-vinylpyridine (II), 4-vinylpyridine (III), and styrene (IV). In compounds II-IV, the absolute values of the ^{13}C–^{1}H spin–spin coupling constants of the terminal carbon of the vinyl group vary in a significant range because of the electronic effect of the substituent. The difference of these spin–spin coupling constants $\Delta J = {}^1J_{C,H_B} - {}^1J_{C,H_A}$ remains practically constant and lies in a narrow range from 6.4 to 6.7 Hz. In these compounds the unshared pair of the pyridine nitrogen is either sterically far from the vinyl group or is absent; therefore, it does not affect the ^{13}C–^{1}H spin–spin coupling constant of the vinyl group.



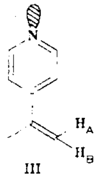
I

$^1J_{C,H_B} = 160{,}3$ Hz
$^1J_{C,H_A} = 155{,}5$ Hz
$\Delta J = 4{,}8$ Hz



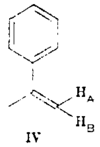
II

$^1J_{C,H_B} = 161{,}1$ Hz
$^1J_{C,H_A} = 154{,}5$ Hz
$\Delta J = 6{,}6$ Hz



III

$^1J_{C,H_B} = 161{,}7$ Hz
$^1J_{C,H_A} = 155{,}0$ Hz
$\Delta J = 6{,}7$ Hz



IV

$^1J_{C,H_B} = 160{,}2$ Hz
$^1J_{C,H_A} = 153{,}8$ Hz
$\Delta J = 6{,}4$ Hz

In compound I, having predominantly an s-cis conformation [2], the C–H_A bond and the unshared pair of nitrogen are sterically close. Because of this, the value of ΔJ decreases jumpwise to 4.8 Hz, which is related to the increase of the spin–spin coupling constant $^1J_{C,H_A}$ because of the additional positive contribution from the unshared pair through the space. A comparison of the values of ΔJ for compound I and II-IV makes it possible to evaluate this contribution as 1.5-2.0 Hz.

Thus, we have found an example of the stereospecific effect of the unshared pair of the pyridine nitrogen on the spin–spin coupling constant $^1J_{CH}$ of the carbon in the γ position with respect to the heteroatom. The observed effect can find important use in studies of the stereochemistry of heterocyclic compounds.

The proton-bound ^{13}C NMR spectra were recorded at room temperature with a Bruker CXP 300 spectrometer (75.4 MHz) in $CDCl_3$, and the concentration of the specimens was 30%. The measurement accuracy for the spin–spin coupling constants was not less than ±0.1 Hz. The spectra were interpreted according to first-order rules.

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PHOTOCHROMIC FULGIDES OF THE INDOLE SERIES

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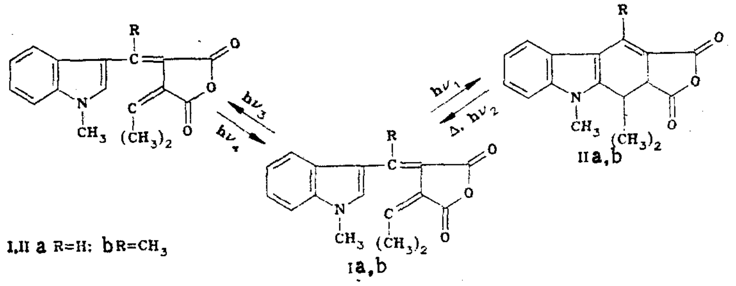
Heterocyclic fulgides have photochromic properties [1, 2]. We have synthesized 1-methyl-3-indolylmethylene-2-isopropylidene-3-[(1-methyl-3-indolyl)alkylidene]succinic anhydrides (fulgides Ia,b) by condensation of 1-methyl-3-formylindole and 1-methyl-3-acetylindole with diethyl isopropylidenesuccinate in the presence of sodium hydroxide with subsequent hydrolysis of the indolyl-substituted isopropylindenesuccinic acid esters and treatment of the resulting dicarboxylic acids with acetyl chloride.



I,II a R=H; b R=CH₃

Ia,b

IIa,b

Fulgide Ia. This compound was obtained in 65% yield and had mp 253-255°C (from o-dichlorobenzene). IR spectrum (mineral oil): 1790, 1745 cm^{-1}. PMR spectrum ($CDCl_3$ in the presence of two drops of CF_3COOH), δ: 1.95 (s, CH_3), 2.10 (s, CH_3), 3.50 (s, NCH_3), 6.80-7.42 (m, 5H), 8.52 ppm (s, CH).

Fulgide Ib. This compound was obtained in 58% yield and had mp 140-142°C (from CCl_4). IR spectrum (mineral oil): 1785, 1745 cm^{-1}. PMR spectrum ($CDCl_3$), δ: 0.88 (s, CH_3), 2.10 (s, CH_3), 2.74 (s, CH_3), 3.80 (s, NCH_3), 7.04-7.64 ppm (m, 5H).

The results of elemental analysis of the compounds obtained were in agreement with the calculated values. Information regarding the structures of the fulgides will be reported later.

Photoinduced changes in the absorption spectra that are associated with photoisomerization relative to the C=C bond and the formation of cyclic form II are observed in the regions of their long-wave absorption bands (λ_{Ia} 380 nm and λ_{Ib} 412 nm) when solutions of fulgides Ia,b are irradiated at 293°K. Cyclic form IIa (λ_{max} 535 nm) is thermally unstable ($\tau \simeq$ 200 msec). At the same time, the analogous IIb form (λ_{max} 545 nm) is thermally stable at normal temperatures and is converted to the original structure only upon photoexcitation.

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