9-ALKENYLCARBAZOLES

II.* ^{1}H AND ^{13}C NMR SPECTRA OF 9-VINYLCARBAZOLES

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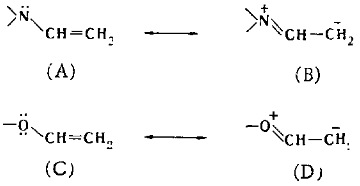
The ^{1}H and ^{13}C NMR spectra of 9-vinylcarbazole and its 3-chloro, 3,6-dichloro, and 3-nitro derivatives were recorded and studied. It is shown that electron-acceptor substituents reduce the shielding of the β-carbon atom and the trans proton of the vinyl group. A good linear correlation between the chemical shifts of these nuclei and the Hammett σ^-_{para} constants with the ρ values (3.78 for $^{13}C_\beta$ and 0.28 for $^1H_{\text{trans}}$) is observed. It was established by comparison of the results with the ^{1}H and ^{13}C NMR spectral parameters for some of the vinyl compounds that the degree of conjugation of the p electrons of nitrogen with the π electrons of the double bond in 9-vinylcarbazoles is lower than in simple vinyl and vinyl phenyl ethers and vinyl acetate.

Formally speaking, 9-vinylcarbazole (9-VC) belongs to the class of enamines in a number of which the contribution of structure B due to conjugation of the unshared electron pair of nitrogen with the π electrons of the double bond (p–π conjugation) is extremely significant and exceeds the fraction of the analogous onium structure (D) in simple vinyl ethers [1].



The increased degree of p-π conjugation in 9-VC, which leads to an increase in the nucleophilicity of the double bond, is in agreement with its high reactivity in cationic reactions, including cationic polymerization [2-4]. A comparison of the quantum-mechanical data [2, 4] also indicates higher electron density on the β-carbon atom of the vinyl group of 9-VC than in the case of simple vinyl ethers. However, the p electrons of the nitrogen atom in the carbazole molecule, on the other hand, are already in conjugation with the aromatic system of rings, and this conjugation should compete and appreciably reduce the p–π conjugation under discussion, since delocalization of the p electrons of nitrogen along the benzene rings of carbazole is extremely substantial and determines its low basic properties [5].

To experimentally solve the problem of the degree of p–π conjugation we recorded and studied the ^{1}H and ^{13}C NMR spectra of 9-vinylcarbazoles I-IV (Tables 1 and 2), since the ^{13}C NMR chemical shift depends directly on the electron density (especially on the π-electron density) on the carbon atom [6-10]; in addition, the ^{1}H NMR [11] and, particularly, the ^{13}C NMR spectra [12-14] made it possible with sufficient completeness to solve the problem of the nature and degree of the p–π conjugation in alkyl and aryl vinyl ethers. Because of the relatively low solubility of II-IV in CCl_4, the ^{13}C NMR spectra of all of the compounds were recorded in acetone solution. The resonance signals of I-IV were assigned on the basis of the spectra of 9-ethylcarbazole [15] and indoles [16] and with allowance for the additive constants of the corresponding substituents in aromatic compounds [17].

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*See [25] for communication I.

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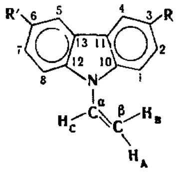

I–IV

I R = R′ = H;
II R = Cl, R′ = H;
III R = R′ = Cl;
IV R = NO_2, R′ = H

Electron-acceptor substituents in the 3 and 6 positions of the carbazole ring in II-IV reduce the shielding of the β-carbon atom and the H_A proton, shifting their signals to weak field as compared with unsubstituted 9-VC, i.e., one observed a decrease in the degree of p–π conjugation or a decrease in the contribution of resonance structure B. It is seen from Fig. 1 that one observes a good linear correlation between the $^{13}C_\beta$ and H_A chemical shifts and the σ^-_{para} substituents; the ρ values determined from the expression $\delta_X - \delta_H = \rho\varepsilon\sigma$ are, respectively, 3.78 (r = 0.997) and 0.28 (r = 0.996). The absence of correlations with the $^{13}C_\alpha$ and H_C chemical shifts indicates the substantial contribution to shielding of these rings by the diamagnetic anisotropy of the C_α=N bond. The absence of correlations with the H_B chemical shifts is explained by the effect on its shielding of the diamagnetic ring currents of the closely situated carbazole ring and also by steric interactions with the ring protons. The ρ value of 3.78 is somewhat lower than the analogous value in the case of p-substituted styrenes (4.73) [18] and phenyl vinyl ethers (5.20) [13]; in general, this indicates the lower transmission properties of the carbazole system. However, it is interesting to note that the $^{13}C_\beta$ chemical shifts in styrenes and phenyl vinyl ethers, in contrast to 9-vinylcarbazoles, correlate with the Hammett σ_{para} constants rather than with σ^-para.

Some vinyl compounds in which one observes conjugation of the electrons of the double bonds with the unshared electrons of the heteroatoms (N, O, S) or with the benzene ring can be arranged in the following order with respect to decreasing shielding of the $^{13}C_\beta$ atom: methyl vinyl ether 85.13 ppm [14], N-vinylpyrrolidone 94.3 [19], N-vinyltetrahydroindole 94.7 [20], phenyl vinyl ether 95.0 [13], vinyl acetate 96.4 [19], 9-VC 101.08, methylthio vinyl ether 107.71 [14], and styrene 112.3 [19]; for comparison, the ^{13}C chemical shift of ethylene is 122.8 [19]. It is difficult to anticipate a single correlation of the $^{13}C_\beta$ chemical shift with the electron density for these vinyl compounds of different classes, but the extremely substantial shift of the $^{13}C_\beta$ signal of 9-VC to weak field indicates lower electron density on its C_β atom as compared with simple vinyl ethers and even phenyl vinyl ether and vinyl acetate. This indicates that delocalization of the p electrons of the nitrogen atoms in 9-VC over the aromatic system prevails over their participation in the p–π conjugation under discussion and renders the contribution of structure B substantially smaller than the contribution observed with ordinary enamines. The contribution of this resonance structure is even less than in the case of N-vinylpyrrolidone, in which there is an electron-acceptor carbonyl group adjacent to nitrogen. This result contradicts the above-mentioned quantum-mechanical data [2, 4], which may raise some doubt, since they give an increase in the electron density on the C_β atom of the vinyl group for a series of N-vinyl derivatives of pyrrole, indole, and carbazole. In fact, however, the condensation of benzene rings with the pyrrole molecule should cause an increase in the degree of delocalization of the p electrons of the nitrogen atom over the entire aromatic system (which finds a distinct confirmation in the decrease in the basicity of the nitrogen atom [5] and in the decrease in the degree of its shielding in the ^{14}N NMR spectra [21]) and should reduce the degree of p–π conjugation, making these compounds even less similar to enamines. This is experimentally confirmed by the substantially greater shielding of the C_β atom in the ^{13}C NMR spectra of N-vinylpyrroles [20] as compared with 9-VC.

A decrease in the shielding of the trans protons of the H_A type for a series of vinyl compounds is observed in the same sequence as for the $^{13}C_\beta$ nucleus: vinyl methyl ether 4.0 ppm [22], N-vinyltetrahydroindole 4.33 [20], vinyl acetate 4.48 [23], 9-VC 4.94, and styrene 5.02 [23]. With allowance for the correlation found between the chemical shifts of the β-vinyl protons and the π-electron density on the C_β atom in various classes of vinyl

TABLE 1. Parameters of the ^1H NMR Spectra of the Vinyl Group of 9-Vinylcarbazoles (I-IV)

Compound	Chemical shift, δ, ppm			J, Hz		
	H_A	H_B	H_C	AC	BC	AB
I	4,94	5,36	7,06	9,45	16,0	0,6
II	5,01	5,31	7,01	9,50	16,0	0,9
III	5,10	5,40	7,04	9,50	16,1	1,0
IV	5,27	5,54	7,11	9,50	16,0	1,0

TABLE 2. Parameters of the ^{13}C NMR Spectra of 9-Vinylcarbazoles

Compound	Chemical shifts, δ, ppm, with respect to tetramethylsilane													
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_{10}	C_{11}	C_{12}	C_{13}	C_α	C_β
I	110.69	126.44	120.77	120,22					139,33	124,01			129,57	101.08
II	112,73	127,30	126,47	121.20	120.01	120.71	126.27	110,94	138.71	124,51	140,19	123.77	129.61	102.21
III	112,46	127.19	126,42	120.56					138,66	124.44			129.80	103,29
IV	111,43	121.20	140,64	116,67	121.74	122,11	128.10	110.62	143,78	124.43	141.93	123.69	129,23	105.72

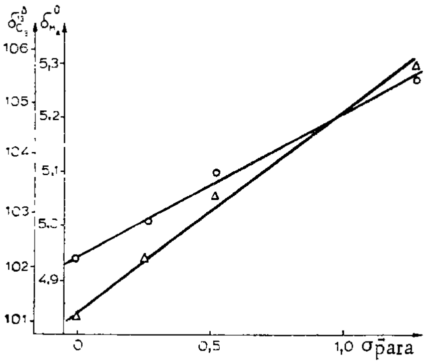

Fig. 1. Dependence of δ_{H_A} and δ^{13} C_β of 9-Vinylcarbazoles I-IV on σ^-_{para}.

compounds [23], it can also be asserted that a decrease in the π-electron density on the C_β atom of the vinyl group also occurs in this series.

It must be noted that the signs of the J_{AB} constants were not specially determined. The s character of the hybridization of the C_β atom increases as the contribution of resonance structure B decreases in the I-IV series (limiting structures A and B have, respectively, sp^2- and sp^3-hybridized C_β atoms), whereas, according to [24], this should lead to an increase in the spin–spin coupling constants between the geminal protons. The J_{AB} constants will consequently have positive signs.

EXPERIMENTAL

The ^1H NMR spectra of 5% solutions of I-IV in carbon tetrachloride were recorded with a BS-487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The ^{13}C NMR Fourier spectra of 10% solutions of the compounds in acetone were recorded with a Bruker HX-90 spectrometer (22.63 MHz) under conditions of complete suppression of the $\{^1H\}-^{13}C$ spin–spin bond; d_6-acetone was added to stabilize the resonance conditions. The chemical shifts are presented relative to tetramethylsilane.

Compounds I-III were synthesized by vinylation of the appropriate carbazole derivatives with vinyl butyl ether in the presence of mercuric trifluoroacetate [25] and were purified by two recrystallizations from methanol. Their purity was monitored by thin-layer chromatography on Silufol plates. Compound IV was synthesized by the method in [26] by pyrolysis of 9-(α-acetoxy)ethyl-3-nitrocarbazole.

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SYNTHESIS AND STEREOISOMERISM OF N-OXIDES OF THE DECAHYDROQUINOLINE SERIES

IV.* ESTABLISHMENT OF THE CONFIGURATION OF EPIMERIC N-OXIDES OF 4-SUBSTITUTED 1,2-DIMETHYLDECAHYDRO-4-QUINOLOLS BY PMR SPECTROSCOPY

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The orientation of the substituents attached to the nitrogen atom in epimeric N-oxides of 1,2-dimethyl-4-ethynyl (vinylethynyl, vinyl, acetyl) decahydro-4-quinolols was established by means of PMR spectroscopy with the aid of the dependence of the chemical shifts of the 3-H_a and 3-H_e protons on the orientation of the N→O bond and the effect of the diamagnetic anisotropy of the C–C and C–H bonds of the rings. It was found that the equatorial methyl group attached to the nitrogen atom resonates at weaker field than the axial methyl group. The quantitative ratio of the epimeric N-oxides in the mixtures was determined.

The present research was devoted to the determination by means of PMR spectroscopy of the orientation of the substituents attached to the nitrogen atom in epimeric N-oxides of 4-substituted 1,2-dimethyl-trans-decahydro-4-quinolols.

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*See [1] for communication III.

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