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PMR AND UV-VIS SPECTROSCOPIC STUDIES ON STRUCTURE OF SOME N-VINYLCARBAZOLES

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Abstract—The PMR spectra are presented of some N-vinylcarbazoles (NVC) i.e. of 3-halogeno-NVC, 3-nitro-NVC, 3,6-dihalogeno-NVC, 3,6-dinitro-NVC, 1,3,6-trihalogeno-NVC and 1,3,6,8-tetra-halogeno-NVC. The chemical shifts show that in both tri- and tetra-substituted NVC derivatives the rotation of the vinyl group is strongly restricted. This group occupies a plane perpendicular to the carbazole ring and this conclusion is substantiated by the UV-VIS absorption spectra of selected NVC derivatives.

Several derivatives of N-vinylcarbazole have been used in the synthesis of a new group of polymers exhibiting semiconducting as well as photosensitive properties. Therefore investigations have been made on both the synthesis and structure of this kind of compound.[1,2]

In the structural studies, among other methods, the high resolution PMR seems to be a very useful tool. The vinyl group of NVC and of its derivatives gives an APX pattern in the PMR in either $CDCl_3$ or DMSO solution. Thus, the methylene protons yield two pairs of doublets in the region of δ5.0–5.8 ppm (in $CDCl_3$) and chemical shift of the methine proton (doublet of doublet) is frequently either overlapped by the signals of the aromatic protons or hidden under them. Their positions are resolved using the INDOR technique which gives also the possibility of assigning relative signs of coupling constants between the protons of the vinyl group,[3,4] although data reported are not consistent with one another.

In this paper studies are presented of the effect of some substituents in carbazole ring of the N-vinylcarbazole on the chemical shift and coupling constants of the vinyl protons.

EXPERIMENTAL

The compounds under study were prepared from commercially available carbazole following methods described in the literature.[1,2,5,6]

Halo-derivatives of N-vinylcarbazole were purified on a chromatographic column and the purity of eluted compounds was additionally proved as described for corresponding halo-derivatives of carbazole.[7] The nitroderivatives were purified by crystallization from benzene (mononitro compounds) and nitromethane (dinitro compounds).

The PMR spectra were recorded at 23° in the $CDCl_3$ soln at a concentration 0.3 M for all NVC, mono- and dihalo-NVC and 0.17 M for all tri- and tetra-halo-NVC and di-nitro-NVC because the latter were not sufficiantly soluble.

It has been proved by recording PMR spectrum of NVC in 0.17 M concentration at both 23° and 60° that such changes in concentration do not affect the chemical shifts of the vinyl protons within the range of experimental error.

All the spectra (Table 1) were recorded with a TESLA BS 487

Table 1. ^1H Chemical shifts and coupling constants for the protons of the vinyl group in NVC and its derivatives†

Compound	Chemical shift δ /ppm/			Coupling constant /Hz/		
	H_X	H_P	H_A	$^2J_{PX}$	$^3J_{AX}$	$^3J_{AP}$
N-Vinylcarbazole	5,04	5,43	7,19	−0,85	9,15	15,90
3-Chloro-NVC	5,06	5,39	7,09	−0,95	9,15	15,85
3,6-Dichloro-NVC	5,08	5,34	6,98	−1,05	9,10	15,85
1,3,6-Trichloro-NVC	5,38	5,38	7,54	−0,60	8,35	15,70
1,3,6-Trichloro-8-bromo-NVC	5,49	5,00	7,40	−0,80	7,50	15,25
3-Bromo-NVC	5,07	5,39	7,09	−0,95	9,15	15,85
3,6-Dibromo-NVC	5,13	5,38	7,02	−1,05	9,15	15,85
1,3,6-Tribromo-NVC /43°C/	5,41	5,35	7,51	−0,70	8,25	15,60
1,3,6,8-Tetrabromo-NVC	5,54	4,99	7,49	−0,80	7,50	15,25
3-Iodo-NVC	5,07	5,38	7,07	−0,85	9,15	15,85
3,6-Diiodo-NVC /55°C/	5,15	5,39	7,03	−1,05	9,05	15,75
3-Nitro-NVC	5,31	5,55	7,11	−1,15	9,00	15,85
3-Nitro-NVC /DMSO, 130°C/	5,40	5,70	7,46			
3,6-Dinitro-NVC* /DMSO, 130°C/	5,58	5,81	7,47	−1,50	9,00	15,60

*The measurement carried out in DMSO at 130°C due to insolubility of the compound in $CDCl_3$. This compound is also sparingly soluble in DMSO at the room temperature.

†The accuracy of the estimation of the coupling constants is ±0.05 Hz in every case.

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C 80 MHz spectrometer using HMDSO as the internal standard. In few cases the measurements were carried out in the DMSO solution at 23° and 130° using DSS as the internal standard.

The UV-VIS absorption spectra of NVC, 3,6-dibromo-NVC, 1,3,6-trichloro-NVC and 1,3,6,8-tetrabromo-NVC were run in the ethanolic solutions at the concentration of about 10^{-4} M.

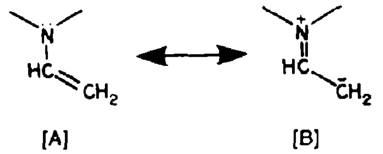
The spectrum of N-vinylcarbazole was additionally recorded in the n-hexane solution at the same concentration.

All the spectra were recorded using the Specord UV-VIS Carl Zeiss Jena device.

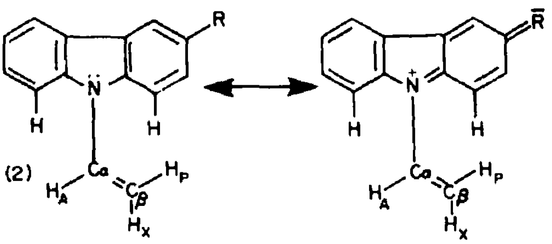
RESULTS AND DISCUSSION

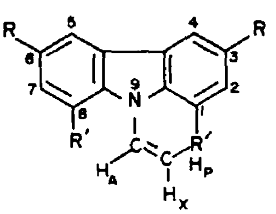
The lone electron pair of the ring N atom of N-vinylcarbazole is conjugated with π electrons of the vinyl double bond and, simultaneously, with the ring π electron system. Therefore, two possible resonance structures 1 and 2 have to be taken into account.

(1)



(2)


R = H, Cl, Br, J


R = H, Cl, Br, J, NO_2
R′ = H, Cl, Br

Filimonov *et al.*[4] have shown for some 3-mono- as well as 3,6-di-substituted N-vinylcarbazoles that a relationship exists between the charge density at C_β atom and both $^{13}C_\beta$ and $^{1}H_X$ chemical shifts. We have found this relationship is not followed if additional substituents in both 1- and 8- positions are present since the substituents influence the $^{1}H_X$ chemical shift for both electronic and steric reasons.

As could be anticipated the effect of the halogen atoms in the 3- and 6- positions on the variation of chemical shifts of the vinyl protons is almost negligible (Table 1). An overall weak inductive effect is reflected by shifting signals of methine proton (H_A) and *cis*-methylene proton (H_X) to the lower field. This seems to be evidence that electron accepting substituents residing in both 3- and 6-positions of the carbazole system decrease the significance of the resonance structure (**1B**) by decreasing the charge densities at the C_β atom and H_X proton. This effect can influence the course of polymerization of N-vinylcarbazole derivatives.[8]

The influence of the inductive effect upon the *trans*-methylene proton (H_P) is difficult to recognize. This proton interacts with protons at both 1 and 8 positions, and such kind interactions may be deduced by analysis of the model of the NVC molecule (Fig. 1). Moreover, steric hindrances in 1,3,6-tri- and 1,3,6,8-tetra-substituted derivatives prohibite free rotation of the vinyl group as can also be deduced from that model.

The inspection of the data in Table 1 reveals that the substitution in the 1 position of NVC results in significant changes in chemical shifts and coupling constants for all vinyl protons. The changes of the PMR spectrum are due to shift of the signals of H_X and H_A protons toward lower field and a decrease in absolute value of geminal coupling constant. Simultaneously, the chemical shifts of both H_X and H_P protons come closer to one another. The course of these changes fits the suggested change of the structure due to restrictions in the free rotation of the vinyl group. The decrease of the relative value of the geminal coupling constant may be interpreted in terms of the electronic effect of electron accepting substituent. This point of view is supported by HMO-theory.[9]

The restriction of free rotation of the vinyl group in 1,3,6,8-tetrahalo-NVC is more pronounced than in 1,3,6-trihalo-NVC. In the PMR spectrum the upfield shift of the signal of the H_P proton can be rationalized in terms of interactions of that proton with the functional groups in both 1 and 8 positions.

We have found that the geminal coupling constant is negative for all cases under study. This observation agrees with the preliminary results of Dambska and Janowski[3] and does not fit the conclusions of Filimonov *et al.*[4]

In order to prove our suggestions on changes of internal structure of the tri- and tetra-halo-NVC derivatives caused by restrictions of free rotation of the vinyl group UV-VIS spectra of selected halo NVC derivatives are measured and roughly interpreted (Figs. 2 and 3).

The spectrum of NVC closely resembles the spectrum of N-ethylcarbazole observed by Okamoto and Kusabayashi[10] who ascribe the bands in order from the shortwavelength region as the $^1B_a \leftarrow {}^1A$, $^1B_b \leftarrow {}^1A$, $^1L_a \leftarrow {}^1A$, and $^1L_b \leftarrow {}^1A$ transitions. However, based on the resemblance of the spectra of all carbazole and other condensed aromatic ring systems such notation may be suspect and demands a more detailed theoretical approach. It is not quite clear whether the band centered in the region of 270 nm or the one in the region 300 nm should be considered as the ^1L_a band and this problem will be the subject of further study.

The substitution of NVC by halogen in both 3- and 6-positions produced bathochromic shifts of the bands (Table 2). This trend reflects the extention of the conjugated π-electron system. The insertion of additional halogen atoms in the 1-position and also in both 1- and 8-positions causes the blue shift of the band at about 270 nm in respect to position of the relevant band in the spectra of both NVC and 3,6-dihalo-NVC. Simultaneously the band at about 300 nm remains unchanged. This influence reflects not only a weak contribution of the halogen atoms in both 1- and 8-positions to the overall π-electron system but suggests the extention of this system is significantly reduced. One of possible explanation of this observation may be due to the steric repulsion of the functional groups out of the plane of molecule.

As it is shown in Figs. 1 and 2 the intensities of the bands at about 245 and 300 nm are practically identical

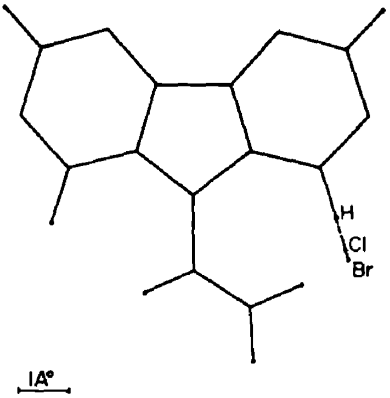


Fig. 1. Model diagram of N-Vinylcarbazole.

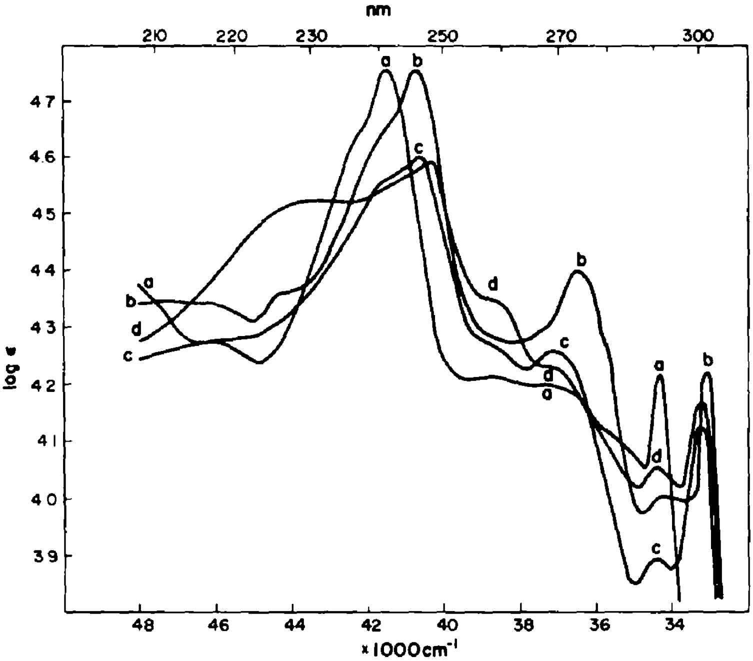


Fig. 2. The UV-VIS absorption spectra in ethanol of NVC and its derivatives.†

†The accuracy in ϵ_{max} is ±4% in every case. [a]N-Vinylcarbazole; [b]3,6-Dibromo-NVC; [c]1,3,6-Trichloro-NVC; [d]1,3,6,8-Tetrabromo-NVC.

Table 2. The UV-VIS spectral bands of NVC and its derivatives†

Compound	${}^1B_a \leftarrow {}^1A$ band			${}^1B_b \leftarrow {}^1A$ band			${}^1L_a \leftarrow {}^1A$ band			${}^1L_b \leftarrow {}^1A$ band		
	λ_{max} /nm/	ϵ_{max}	$\lg\epsilon_{max}$	λ_{max} /nm/	ϵ_{max}	$\lg\epsilon_{max}$	λ_{max} /nm/	ϵ_{max}	$\lg\epsilon_{max}$	λ_{max} /nm/	ϵ_{max}	$\lg\epsilon_{max}$
a^1	242,0	56000	4,75	274,0	14700	4,17	291,5	19400	4,29	339,0	6000	3,78
a	241,5	57000	4,76	272,0	15300	4,18	291,5	16500	4,22	340,0	4400	3,64
b	245,5	57000	4,76	274,0	25800	4,41	302,0	16500	4,22	358,5	3400	3;53
c	246,5	40000	4,60	269,5	19500	4,29	301,0	13500	4,13	360,5	3300	3,52
d	248,0	39500	4,60	270,5	17000	4,23	301,0	14800	4,17	356,0	3650	3,56

†The accuracy in ϵ_{max} is ±4% in every case.

[a'] N-Vinylcarbazole in n-hexane; [a]N-Vinylcarbazole in ethanol; [b]3,6-Dibromo-NVC in ethanol; [c]1,3,6-Trichloro-NVC in ethanol; [d]1,3,6,8-Tetrabromo-NVC in ethanol.

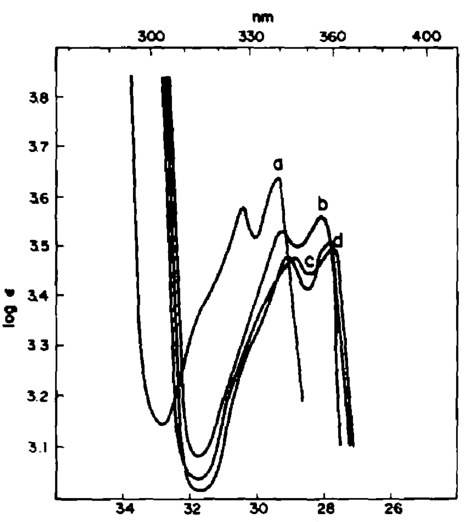


Fig. 3. The UV-VIS absorption spectra in ethanol of NVC and its derivatives (continuation of Fig. 2).

for both NVC and 3,6-dibromo-NVC but decrease in the spectra of both 1,3,6-trichloro- and 1,3,6,8-tetra-bromo-NVC.

On the other hand the substitution of the NVC system increases the intensity of the band at about 270 nm in all cases. However a gradual decrease of the intensity of that band is observed as the number of introduced halogen atoms increases. Since the twist of the vinyl group out or the plane of molecule seems to be involved the $\cos^2\theta$ law[11] allow an estimate to be made of the angle of the twist of that group. This law applies to the intensity changes of the ^1L_a-band and since we have some doubt which of two, i.e. 270 and 300 nm bands is ^1L_a-band calculations were carried out for both bands. The results are as follows: In the case of the 270 nm band the angles of the twist are 29°37′ and 35°44′ for 1,3,6-trichloro-NVC and 1,3,6,8-tetrabromo-NVC, respectively, whereas for the 300 nm band corresponding values are 25°14′ and 18°43′, respectively.

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