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9-ALKENYLCARBAZOLES.

10.* ^{13}C NMR SPECTRA OF 9-VINYL- AND cis- AND trans-9-PROPENYLCARBAZOLES

V. D. Filimonov, V. A. Anfinogenov,
and S. G. Gorbachev

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The ^{13}C NMR spectra of a number of ring-substituted 9-vinylcarbazoles and cis- and trans-9-propenylcarbazoles were studied. It was found that the $C_β$ chemical shifts of the vinyl atoms of these compounds correlate satisfactorily with the $σ_p$ constants of the substituents in the 3 and 6 position of the carbazolyl rings; the slopes of the straight lines increase in the order 5.84, 7.68, 9.56. The inductive and conjugation components of the effect of the substituents on the chemical shifts of the $C_β$ atoms were evaluated. It follows from the results obtained that the effects of p–π conjugation are realized not only in the relatively planar isomers but also in the nonplanar cis isomers of 9-alkenylcarbazoles.

Previously by means of ^{13}C NMR spectroscopy for the study of the effects of p–π conjugation in 9-vinylcarbazole (Ia) and its derivatives with electron-acceptor substituents in the heterocyclic fragment (Ic-e) we evaluated the effect of substituents on the shielding of vinyl $C_β$ atoms [2]. In the present paper we present the results of an NMR spectral study of a series of substituted (in the 3 and 6 positions of the carbazolyl ring) cis (IIa-d) and trans (IIIa-d) isomers of 9-propenylcarbazoles. We also recorded the spectrum of 3-methyl-9-vinylcarbazole (Ib) in order to expand the series of substituted vinylcarbazoles I. The results are examined in conjunction with the data in [2] in order to compare the effects of transmission of the effects of the X and Y substituents on the C=C group in all three series of alkenylcarbazoles I-III.

Compounds I-III constitute two conformationally different groups. The trans isomers (III) are isosteric (relative to the mutual orientation of the planes of the carbazolyl ring and the C=C bond) with respect to I. The existence of two conformations with angles of deviation from coplanarity of the ring and the C=C bond of 2.6 and 14° has been established for vinylcarbazole Ia by x-ray diffraction analysis [3]. Thus there is a small degree of noncoplanarity as a result of repulsion of the cis proton of the methylene group and the ring 1-H and 8-H protons. Taking into account the known indeterminacy in the application of the crystallographic parameters of the substances to their solutions, one may tentatively adopt

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*See [1] for Communication 9.

S. M. Kirov Tomsk Polytechnic Institute, Tomsk 634004. I. I. Polzunov Altai Polytechnic Institute, Barnaul 656099. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1640-1644, December, 1982. Original article submitted February 22, 1982.

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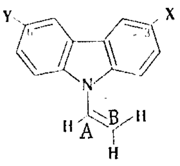
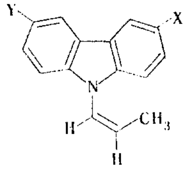
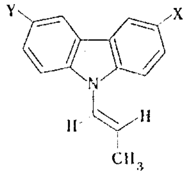


I a-e



II a-d



III a-d

Ia X=Y=H; b X=CH_3, Y=H; c X=Cl, Y=H; d X=Y=Cl; e X=NO_2, Y=H; IIa X=Y=H;
b X=C_2H_5, Y=H; c X=Y=Cl; d X=NO_2, Y=H; IIIa X=Y=H; b X=C_2H_5, Y=H;
c X=Cl, Y=H; d X=Y=Cl

a configuration that is similar to that of vinylcarbazole for trans isomers III, designating it arbitrarily as a planar configuration. In contrast to carbazoles I and III, cis isomers II certainly cannot exist in a planar configuration. According to data from the UV spectra, the deviation from coplanarity for propenylcarbazole IIa is 30-41° [4].

The ^{13}C NMR chemical shifts of I-III are presented in Table 1. As a consequence of the low solubilities of the nitro derivatives in nonpolar solvents, the spectra of all of the compounds were recorded in 10% solutions in deuteroacetone. The assignment of the resonance signals was made on the basis of experiments with selective suppression of the spin—spin coupling with the protons using the additive constants of the substituents in the aromatic compounds [5], the relative intensities of the signals, and previous results [2, 6]. Compounds IIa and IIIa-d had 100% isomeric purity, while cis isomers IIc, d contained 5-8% of the trans isomers, which did not interfere with the assignment of the signals. However, the IIb derivative contained ~20% (according to the PMR spectral data) 3-ethyl-9-allylcarbazole, in connection with which the assignment of the low-intensity signals of the quaternary $C_{(3)}$ $C_{(8a)}$, and $C_{(9a)}$ atoms in this compound is not absolutely reliable.

Of the results obtained, the following are the most important in our opinion. The 2.42 ppm weak-field shift of the signal of the C_B atom of cis isomer IIa as compared with trans isomer IIIa, in agreement with previous data in a nonpolar solvent (CCl_4) [4], unambiguously establishes a decrease in the electron density on this atom because of appreciable suppression of the p—π conjugation as a consequence of the noncoplanarity. This fact first of all per se indicates the existence of conjugation in isomer IIIa and, second, is in agreement with the close-to-planar structure of this isomer (and vinylcarbazole Ia) in solutions. If this were not the case, if one were to assume an angle of deviation from coplanarity in IIIa close to 90°, the cis-methyl group should not have caused such an appreciable change in the chemical shift of the C_B atom and the very pronounced decrease in the activity of the C=C bond of cis isomer IIa in hydration [7]. Indirect evidence in favor of the coplanar structure of vinylcarbazole Ia is also provided by the data in [8], in which it is shown that substituents (halogens) in the 1 and 8 positions of the carbazolyl fragment appreciably deshield the methylene protons of the N-vinyl group in the PMR spectra as a result of deviation of the vinyl group from coplanarity with the ring. In addition to this, the data from the ^{13}C NMR spectra and the result of quantum-chemical calculations of N-vinylpyrroles, which show that conformations with an angle of deviation from coplanarity of the pyrrole ring and the C=C bond of 55° are characteristic for the 2-substituted compounds, whereas this angle is 90° for the 2,5-disubstituted compounds [9], contradict the conclusion that carbazoles I and III have planar structures. Vinylcarbazole Ia, inasmuch as it is formally a tetrasubstituted N-vinylpyrrole, should, according to these results, exist in an orthogonal confirmation, which is not in agreement with the x-ray diffraction data [3] and contradicts the results presented above, which indicate that Ia and IIIa most likely have planar structures. In order to explain this contradiction one must assume that the phenylene rings annelated to the pyrrole ring interact sterically with the vinyl group to a lesser degree than the alkyl groups in the 2 and 5 positions of pyrrole or that attractive nonbonding interactions exist between the phenylene rings and the vinyl group in carbazoles Ia and IIIa. These assumptions are in agreement to a certain extent with the fact that the predominant conformations in N-formylindole and, particularly, in N-formyl-2,3-dimethylindole are conformations with a syn orientation of the carbonyl group and the phenylene ring (65 and 90%, respectively) [10].

The chemical shift of the C_B atom of cis-propenylcarbazole (IIa) is 119.57 ppm, i.e., this atom is shielded to a greater extent than the corresponding vinyl atoms of cis-2-butene (123.3 ppm) [5] or cis-propenylbenzene (126.9 ppm) [11]. At the same time, one should have expected the reverse of this pattern if the effect of p—π conjugation, which increases the

TABLE 1. ^{13}C NMR Chemical Shifts (δ, ppm relative to tetramethylsilane) of 9-Alkenylcarbazoles

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9a)}$	$C_{(4a)}$	$C_{(8a)}$	$C_{(4b)}$	C_A	C_B	CH_3
Ia [2]	110,69	126,44	120,22	120,77					139,33	124,01			129,57	101,08	
Ib	110,18	126,60	127,82	120,89	120,11	119,99	126,30	110,60	136,63	123,90	139,20	124,00	129,10	100,02	
Ic[2]	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	
Id[2]	112,46	127,19	126,42	120,56					138,66	124,44			129,80	103,29	
Ie [2]	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	
IIa	110,73	126,48	120,28	120,76					140,83	123,62			126,70	119,57	13,58
IIb	110,00	126,59	126,91	120,70	120,28	119,47	126,11	110,78	139,12	123,70	138,89	123,11	126,11	118,82	13,50
IIc	112,35	127,23	125,80	120,92					139,75	123,94			128,23	123,03	13,42
IId	111,54	121,68	142,18	117,42	121,80	121,89	128,21	110,62	143,92	123,69	142,18	123,40	129,23	125,89	13,36
III a	110,78	126,64	120,60	120,60					140,23	123,99			124,59	117,15	15,47
IIIb	109,14	126,69	127,17	121,30	120,12	119,31	126,11	110,69	138,16	123,93	139,96	123,02	124,64	116,05	15,40
IIIc	112,15	126,49	125,79	121,10	121,10	120,80	127,51	111,07	138,68	125,36	140,90	123,04	124,44	119,53	15,70
IIId	112,52	127,36	126,12	120,94					139,44	122,96			124,23	121,73	15,54

electron density on the C_B atom, were completely suppressed in cis isomer IIa. In the absence of a positive mesomeric effect of the carbazolyl fragment, its appreciable negative inductive effect (Taft constant σ^* for the 9-carbazolyl group is 1.55 [12]), which deshields the C_B atom, should have become dominant. Furthermore, the range of changes in the chemical shifts of the C_B atoms of isomers IIIa-d exceed the range for the C_A atoms by a factor of more than two (7.07 and 3.12 ppm, respectively). A similar pattern is also observed for the changes in the chemical shifts of the C_B and C_A atoms of trans isomers IIIa-d (5.68 and 0.41 ppm) and vinylcarbazoles Ia-e (5.70 and 0.7 ppm). Greater sensitivity to the effect of substituents of atoms that are more remote from them is characteristic for conjugated systems. Thus the facts presented above compel us to acknowledge that although conjugation in cis isomer IIa is markedly inhibited sterically, this inhibition is not complete. At the very least, residual signs of conjugation do appear in the NMR spectra.

The chemical shifts of the vinyl C_B atoms of all three series of compounds I-III correlate satisfactorily with the σ_p constants of the X and Y substituents. The parameters of the corresponding regression equations

$$\Delta\delta C_B = \delta C_B{}^X - \delta C_B{}^H = a + \rho\sigma_n. \tag{1}$$

are presented in Table 2.

One's attention is directed to the rather significant ρ values for all three series of investigated compounds. Thus, for example, the slopes of the analogous dependences for styrenes are 5.5 (scaled with respect to the data in [13]), whereas they are 5.21 and 6.64, respectively, for cis- and trans-propenylbenzenes [11], although in these cases the effect of the substituents from the para positions of the phenyl rings on the C_B atoms is transmitted through six bonds, i.e., over a shorter distance than in alkenylcarbazoles I-III. This indicates the better transmission properties of alkenylcarbazole molecules as compared with styrene molecules. At the same time the conductivity of the carbazolyl ring relative to the effect of substituents on the pK_a values of 9-carbazolylacetic acids (the absence of conjugation between the reaction center and the ring) is appreciably lower than that of the phenyl ring [12]. Thus the introduction of vinyl and cis- and trans-propenyl groups at the nitrogen atom of the carbazole fragment leads to a pronounced increase in the π polarizability of the molecule as a whole, which constitutes additional evidence in favor of the existence of conjugation between the C=C bond and the ring in I-III. Similar intensification of the π polarizability of the heterocyclic skeleton by the vinyl group was previously observed for N-vinylpyrroles [14].

The increase in the ρ values in the order I < II < III is interesting. It is evident that the noncoplanarity of cis isomers II should also lead to substantial suppression of the overlapping of the p and π orbitals, as demonstrated in the present paper and in [4, 6, 7]. In this case one should expect difficulties in transmission of the effect of the X and Y substituents via a conjugation mechanism, and this is established by the smaller ρ value for cis isomers IIa-d (7.68) as compared with trans isomers IIIa-d (9.56). The interpretation of the smallest ρ coefficient for Ia-e is not so unambiguous. It is known that obvious parallelism between the effect of substituents in olefins and substituted benzenes is observed in many cases [15]. However, the conductivity of the phenyl ring relative to the effect of substituents on the chemical shifts of the p-carbon atoms increases when there is a

TABLE 2. Parameters of Regression Eqs. (1) and (2)

Compound	a	ρ	ρ_I	ρ_R	r	s
I	−0,12	5,84			0,995	0,24
II	0,18	7,68			0,998	0,28
III	0,20	9,56			0,998	0,18
I			5,41	7,08	0,9993	0,12
II			7,23	8,71	0,9992	0,22
III			8,60	8,75	0,9999	0,07

methyl group in the para position relative to the substituents as compared with monosubstituted benzenes. Thus the ρ values in the correlation with the σ_p constants for 4-X-toluenes are −13.18 [16] as against −11.4 for benzenes [5]. An increase in the conductivity of some vinyl aromatic and vinyl heteroaromatic molecules is also similarly observed when a terminal methyl group is introduced. Thus, for example, the ρ values for styrenes and propenylbenzenes have already been presented above. However, the ρ values in the δC_B–δ_p correlation for p-phenyl vinyl ethers are 4.58* [17] (4.84 according to the data in [18]), as compared with 5.0 and 5.2, respectively, for cis- and trans-p-phenyl propenyl ethers [19]. Thus, although the number of such examples in the literature is small, it may be concluded that the intensification of the transmission properties of the vinyl derivatives (at least those with donor substituents) when a β-CH_3 group is introduced is more likely the rule rather than the exception and apparently does not depend on the degree of conjugation of the substituents with the vinyl group. In order to evaluate the relative fraction of the inductive and resonance factors of the effect of the X and Y substituents on δC_B we separated the σ_p effects of the substituents into inductive and resonance effects by means of a three-parameter correlation of $\Delta\delta C_B$ with the σ_I and σ_R^0 constants. The parameters of correlation Eqs. (2) are presented in Table 2. It is clearly apparent that the absolute values of ρ_I and ρ_R increase

$$\Delta\delta C_B = \rho_I\sigma_I + \rho_R\sigma_R^0 \qquad (2)$$

in the same order as the ρ values presented above, i.e., in the order I < II < III; however, the ρ_R/ρ_I ratio is highest (1.31) for vinylcarbazoles Ia-e, which constitute evidence for the large fraction of the resonance component of the effect of the substituents in conformity with the high degree of conjugation in I as compared with propenylcarbazoles II. However, in the case of trans isomers IIIa-d one observes an intimate linear relationship in the pair correlations between the arguments of Eqs. (2). The coefficients of the multiple correlation in this case are therefore statistically indeterminate, just as in the comparison of the ρ_P/ρ_I ratios for III (1.02) with the ratios for II and I (1.20 and 1.31, respectively).

EXPERIMENTAL

The ^{13}C NMR spectra of 10% solutions of I-III in deuteroacetone were recorded with a Brucker HX-90 spectrometer (22.63 MHz) under conditions of complete and selective suppression of the spin–spin coupling with the protons; the chemical shifts were measured with an accuracy of ±0.05 ppm.

Compound Ib was synthesized by vinylation of 3-methylcarbazole with vinyl butyl ether in the presence of mercury trifluoroacetate [20]. Compounds IIa-d and IIIa-d were obtained by the methods in [4, 6], respectively.

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UNSATURATED CHLORO-SUBSTITUTED DINITRILES IN THE SYNTHESIS OF PORPHYRAZINES

V. N. Kopranenkov, L. S. Goncharova,
L. E. Marinina, and E. A. Luk'yanets

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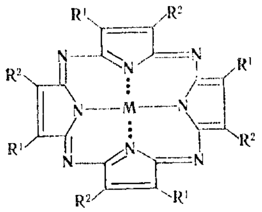
Chloro- and alkoxy-substituted porphyrazines were obtained in the reaction of mono- and dichloromaleo(fumaro)nitriles with metal chlorides or alkoxides. The structures of the synthesized compounds were confirmed by their electronic absorption spectra.

The introduction of halogen atoms into the benzene rings of phthalocyanines is widely used for the preparation from them of photostable green pigments. In the present communication we describe the synthesis of previously unknown chloro-substituted porphyrazines — structural analogs of phthalocyanines — by condensation of mono- (I) and dichloromaleo(fumaro)nitrile (II) with metal chlorides and alkoxides. Dinitriles I and II were also the starting compounds in the synthesis of alkoxy-substituted porphyrazines.



III M=VO, R^1=Cl, R^2=H; IV M=VO, $R^1=R^2$=Cl; V M=Mg, $R^1=OC_5H_{11}$, R^2=H; VI M absent

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