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^{13}C NMR SPECTRA OF 9-METHYLCARBAZOLES AND ELECTRON CONDUCTIVITY OF THE CARBAZOLE RING

V. D. Filimonov, T. A. Filippova,
V. P. Lopatinskii, and M. M. Sukhoroslova

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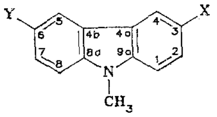
The effect of substituents in the ring of 9-methylcarbazoles on the ^{13}C NMR chemical shifts was determined. Correlation relationships between the inductive and resonance constants of the substituents and the chemical shifts were found. The transmission properties of the carbazole ring with respect to the electronic effects of substituents in the 3 position were evaluated on the basis of the results obtained. Nonadditivity of the effects of the substituents on the NMR chemical shifts within the limits of one phenyl ring of carbazole relative to monosubstituted benzenes was observed.

The chemical shifts in the ^{13}C NMR spectra may serve as a measure of the electron densities on the carbon atoms [1, 2]. We determined the ^{13}C NMR chemical shifts of 9-methylcarbazole (Ia) and a number of 3,6-disubstituted 9-methylcarbazoles (Ib-g) in order to evaluate the degree of transmission of the electronic effects of substituents X and Y through the carbazole ring.



I a-g

I a X=Y=H; b X=CH_3, Y=H; c X=CH_3CO, Y=H; d X=CF_3CO, Y=H; e X=Cl, Y=H; f X=NO_2, Y=H; g X=Y=CH_3CO

To minimize the effect of the solvent the NMR spectra of Ia-g were recorded in a slightly polar solvent ($CDCl_3$) at low concentrations (4% for Ia-e, g and 2% for If). The ^{13}C chemical shifts are presented in Table 1 along with the ^{1}H NMR chemical shifts of the signals of the methyl groups of the same compounds (3% solutions in $CDCl_3$). The assignment of the ^{13}C NMR signals of methylcarbazole Ia and symmetrically substituted derivative Ig on the basis of the previously obtained results from the NMR spectra of 9-alkenylcarbazoles [3] and data on selectively deuterated carbazoles [4] does not present any difficulties. However, the carbon atoms of the two phenylene rings in 3-substituted Ia-f are nonequivalent. Experiments with selective suppression of the spin—spin coupling with the protons were used, the relative intensities of the signals were taken into account, and the obvious assumption that substituents X should have a greater effect on the change in shielding of the nuclei in the substituted ring was made in these cases for assignment of the signals. In addition, the additive constants of substituents X in aromatic compounds [5] were used in the assignment of the chemical shifts of the atoms of the substituted ring.

S. M. Kirov Tomsk Polytechnic Institute, Tomsk 634004. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 204-209, February, 1984. Original article submitted June 29, 1983.

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TABLE 1. ^{13}C NMR Chemical Shifts (δ, ppm) of 9-Methylcarbazoles (solutions in $CDCl_3$)

Compound	X	Y	$C_{(1)}$, $C_{(8)}$	$C_{(2)}$, $C_{(7)}$	$C_{(3)}$, $C_{(6)}$	$C_{(4)}$, $C_{(5)}$	$C_{(9a)}$, $C_{(8a)}$	$C_{(4a)}$, $C_{(4b)}$	CH_3	^1H NMR (CH_3)
1a	H	H	108,13	125,39	118,60	120,00	140,82	122,53	28,51	3,71
1b	CH_3	H	107,93 108,18	126,81 125,29	127,87 118,38	120,08 120,08	139,17 141,05	122,44 122,70	28,75	3,70
1c	CH_3CO	H	107,32 108,40	125,66 125,66	128,10 119,41	120,92 119,84	142,87 140,98	122,43 121,80	28,46	3,73
Id	CF_3CO	H	108,90 108,24	126,80 127,44	110,83 120,27	129,29 120,49	144,27 141,36	123,29 122,37	28,73	3,77
Ie	Cl	H	109,00 108,35	125,23 126,04	124,00 118,87	120,11 119,57	138,83 141,04	123,51 121,51	28,57	3,69
If	NO_2	H	109,25 107,80	121,40 127,28	140,44 120,69	116,95 120,69	143,73 141,96	122,50 122,25	29,33	3,80
Ig	CH_3CO	CH_3CO	108,02	126,15	128,85	120,92	143,46	121,89	28,78	3,77

We have previously determined the inductive constants of the 9-carbazolyl fragment and a number of related N-hetaryl fragments by measuring the pK_a values of the corresponding N-hetarylacetic acids [6]. The selection of 9-methylcarbazoles as the subjects of this research was due, in particular, to the fact that the ^{13}C and ^1H NMR chemical shifts in RCH_3 can serve as a measure of the inductive effect and the effective electronegativities of the R fragments [1, 7]. The pK_a data show the following order of increase in the —I effect of N-hetaryl rings: phenothiazinyl < carbazolyl < indolyl [6]. The following order of increase in the degree of shielding of the CH_3 groups in the ^{13}C NMR spectra is observed in the case of N-methyl derivatives of the same heterocycles: N-methylphenothiazine 35.2 [8], N-methylindole 32.1 [9], and N-methylcarbazole 28.57 ppm. Thus there is no correspondence between the pK_a data and the NMR data, which show that the carbazolyl group has the weakest negative inductive effect. Taking into account the similarity in the structures of all three of the heterocycles under discussion it is difficult to explain such strong shielding of the methyl group of carbazole Ia by means of the effects of magnetic anisotropy. A scale model of methylcarbazole Ia shows that the methyl group is not free from steric interactions on the part of the 1- and 8-H protons. The existence of steric compression between the CH_3 group and the $C_{(1)}$ and $C_{(8)}$ atoms through the 1- and 8-H protons finds confirmation in the appreciable shielding (108.13 ppm) of the $C_{(1)}$ and $C_{(8)}$ atoms of methylcarbazole Ia relative to carbazole, for which the chemical shifts of the $C_{(1)}$ and $C_{(8)}$ atoms are 110.8 ppm; in addition, the ^1H NMR chemical shift of the CH_3 groups of N-methylindole is 3.37 ppm [10], i.e., it lies at stronger field as compared with the signal of methylcarbazole (Table 1). The opposite (in sign) shift of the chemical shifts of the carbon and hydrogen nuclei is characteristic for a C—H bonds that experience steric strain on the part of the hydrogen atom [5]. These results show that the steric component makes a pronounced contribution to shielding of the CH_3 group of methylcarbazole Ia, which makes it impossible to use this chemical shift as a measure of the purely inductive properties of heterocyclic rings.

Substituents X and Y have a relatively small and irregular effect on the ^{13}C (and ^1H) NMR chemical shifts of the CH_3 groups of methylcarbazoles Ia-g (Table 1). At the same time, the electronic effects of substituents X and Y are transmitted rather effectively through the nitrogen atom of the carbazolyl ring, thereby affecting the ^{13}C NMR chemical shifts of the $C_{(\beta)}$-vinyl atoms of 9-alkenylcarbazoles [3] and the acidic properties of 9-carbazolylacetic acids [11] in a regular way. In the case of methylcarbazoles Ia-g it is possible to assume that they exist in conformations with different percentages of eclipsed and skewed interactions of the C—H bonds of the CH_3 groups and the plane of the ring. Under this assumption the discussed steric contribution to the shielding of the methyl groups will not be constant, thereby ensuring irregular changes in the chemical shifts. This interpretation is similar to the explanation of the nonadditivity of the effects of substituents in anisoles and their seleno and thio analogs [12].

An alternative explanation of the constancy of the chemical shifts of the methyl groups of Ia-g in contrast to the extremely appreciable effects of substituents X and Y on the pK_a values of 9-carbazolylacetic acids [11] is based on the analysis carried out in [13], from which it follows that in the case of RCH_3 derivatives the inductive effects of substituents

TABLE 2. Parameters of Regression Equations $\Delta\delta C_i = a + \rho\sigma$ and $\Delta\delta C_i = a + \rho_I\sigma_I + \rho_R\sigma_R$ ($\Delta\delta C_i = \delta C_i^x - \delta C_i^y$) for Methylcarbazoles Ia-f

Eq. No.	C_i	Constants	a	ρ	ρ_I	ρ_R	r	s
1	$C_{(9a)}$	σ_p^+	−0,76	4,94			0,951	0,82
2	$C_{(9a)}$	σ_p	−0,99	5,16			0,882	1,24
3	$C_{(9a)}$	σ_I, σ_R^0	−0,04		1,21	13,18	0,9985	0,17
4	$C_{(6)}$	σ_p	−0,02	2,23			0,964	0,28
5	$C_{(6)}$	σ_p^+	0,15	1,93			0,937	0,36
6	$C_{(6)}$	σ_I, σ_R^0	0,05		2,05	3,02	0,9805	0,24
7	$C_{(7)}$	σ_m	−0,10	2,76			0,941	0,35
8	$C_{(7)}$	σ_p	0,06	2,13			0,923	0,40
9	$C_{(7)}$	σ_p^+	0,25	1,79			0,870	0,51
10	$C_{(7)}$	σ_I, σ_R^0	0,02		2,45	2,05	0,9593	0,34
11*	$C_{(9a)}$	σ_p^+	−0,22	6,73			0,972	0,84
12*	$C_{(6)}$	σ_p	0,06	2,29			0,996	0,11

*Correlation data for 3-substituted 9-vinylcarbazoles calculated from the ^{13}C NMR chemical shifts in [3].

R are transmitted chiefly via the σ bonds, whereas transmission of the inductive effect through space dominates in RCH_2COOH.

Before we turn to a discussion of the effect of substituents X on the chemical shifts of the ring carbon atoms of methylcarbazoles Ia-f we must estimate the extent to which these chemical shifts actually reflect the electron distribution. Quantum-chemical calculations of carbazole (see [14]) predict the following order of decrease in the electron densities: $C_{(1)} > C_{(3)} > C_{(2)} > C_{(4)}$. However, the order of decrease in the shielding by the carbon atom of methylcarbazole Ia (Table 1) differs as follows: $C_{(1)} > C_{(3)} > C_{(4)} > C_{(2)}$. The anomalous shielding of the $C_{(4)}$ atom is, in all likelihood, due to mutual steric strains between the $C_{(4)}$ and $C_{(5)}$ atoms. We demonstrated above that the steric factor makes an appreciable contribution also to shielding of the $C_{(1)}$ and $C_{(8)}$ atoms. Thus, of the carbon atoms of the carbazole ring that are bonded to protons, only the chemical shifts of the $C_{(3)}$ [$C_{(6)}$] and $C_{(2)}$ [$C_{(7)}$] atoms adequately reflect the electron densities.

To correlate the ^{13}C NMR chemical shifts with the effects of substituents we used the differences in the chemical shifts of the atoms of substituted methylcarbazoles and unsubstituted methylcarbazole Ia: $\Delta\delta C_i = \delta C_i^X - \delta C_i^H$. The parameters of the regression equations found are presented in Table 2. The chemical shifts of the $C_{(9a)}$ atoms in methylcarbazoles Ia-f correlate well with the Brown σ_p^+ constants of substituents X [Eq. (1)]; however, the correlations with the Hammett σ_p constants are appreciably poorer [Eq. (2)]. In this respect, the qualitative effect of substituents X on the shielding of the $C_{(9a)}$ atoms is similar to the effect of substituents on the chemical shifts of the p-carbon atoms in monosubstituted benzenes, for which better correlations are also observed with the σ_p^+ constants [2, 5]. These data demonstrate directly for the first time that complete polar conjugation of the substituents within the limits of one phenylene ring occurs in the carbazole series. However, the transmission capacity of the phenylene ring of methylcarbazoles for the transmission of electronic effects from the 3 position to the 9a position is lower by a factor of approximately two than in the case of the phenylene ring in monosubstituted benzenes, in which $\rho = 9.51$ [15].* At the same time, the conductivity of the phenylene ring in p-substituted dimethylanilines $XC_6H_4NMe_2$ ($\rho^+ = 5.54$) is very close to the conductivity of the phenylene ring of methylcarbazoles ($\rho^+ = 4.94$). A good linear correlation ($r = 0.994$, $s = 0.27$) with a slope close to unity ($\rho = 0.90$) exists between the $\Delta\delta C_{(9a)}$ and $\Delta\delta C_p$ values of dimethylanilines, whereas the corresponding correlation with the $\Delta\delta C_p$ values in monosubstituted benzenes is appreciably poorer ($r = 0.983$). Consequently, from the point of view of the conductivity of the electronic effects of substituents from the 3 position to the 9a position, the phenylene ring of carbazoles is similar to the dimethylaniline ring, and nonadditivity of the effects of the substituents on the $\Delta\delta C_{(9a)}$

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*For the $\Delta\delta C_p$ correlation we used the chemical shifts of benzenes and N,N-dimethylanilines that have substituents X (without a trifluoroacetyl group) in common with Ia-c, e, f and were obtained under conditions of low concentrations of the substances in $CDCl_3$ [15], i.e., under conditions that were most comparable to ours.

values in carbazoles Ia-f relative to monosubstituted X on the $\Delta\delta C_p$ values in 1,4-disubstituted benzenes XC_6H_4Y is determined first and foremost by the resonance effect of Y [15]. From this position the observed approximate additivity of the effect of substituents X in methylcarbazoles and dimethylanilines (the NMe_2 group has a strong positive mesomeric effect) is satisfactorily explained by the π-surplus character of the carbazole ring [14]. In this connection it is important to emphasize that extending the concept of the nonadditive effect of substituents on the ^{13}C NMR chemical shifts in 1,4-disubstituted benzenes [15] to heterocyclic compounds leads to the conclusion that the transmission properties of heterocycles depend on their π-surplus and π-deficient character.

Better linear dependences of the $\Delta\delta C_{(9a)}$ values on the electronic effects of substituents X are obtained when the inductive and resonance characteristics are taken into account simultaneously [Eq. (3)]. A comparison of the ρ_I and ρ_R values obtained with the analogous data for 1,4-disubstituted benzenes again indicates the monotypic character of the mechanisms of the electronic conductivity of the phenylene ring of carbazole and the ring of dimethylanilines ($\rho_I = 1.9$, $\rho_R = 12.6$ [15]) and an appreciable difference from the benzene ring ($\rho_I = 4.6$, $\rho_R = 21.5$ [15]).

At present there are no direct quantitative data on the transmission of the effects of substituents from one phenylene ring to another in the ground electronic state of carbazole. The transmission of these effects may be realized through the nitrogen atom (the "diphenylamine" pathway) or through the biphenyl bond, whereas the inductive component of the electronic effects can also be transmitted directly through space. The data in Table 1 show that the degree of shielding of the $C_{(6)}$ and $C_{(7)}$ atoms, free from steric effects, in contrast to the $C_{(5)}$ and $C_{(8)}$ atoms, changes appreciably under the influence of substituents X in Ia-f; the $\Delta\delta C_{(6)}$ values correlate with the σ_p constants of the substituents in this case [Eq. (4)]. This dependence constitutes evidence in favor of predominance of the "diphenylamine" pathway of transmission of the effects of substituents, since the $C_{(6)}$ atom is in the para position relative to the nitrogem atom. In conformity with this conclusion, the $\Delta\delta C_{(7)}$ values, which pertain to substituents in the meta position relative to the nitrogen atom, correlate better with the σ_m constants of substituents X than with σ_p, and correlations of the $\Delta\delta C_{(7)}$ values with the σ_p^+ constants [Eqs. (8) and (9)] of absolutely unsatisfactory quality are observed. The best dependences of $\Delta\delta C_{(6)}$ and $\Delta\delta C_{(7)}$ are observed with the σ_I and σ_R° constants [Eqs. (6) and (10)]. On the basis of the smaller influence of resonance effects in benzenes on $\Delta\delta C_m$ than on $\Delta\delta C_p$ [15], the appreciable decrease in the ρ_R value for the $C_{(7)}$ position as compared with the $C_{(6)}$ position is also a confirmation of predominance of the "diphenylamine" pathway for transmission of the effects of substituents from the 3 position of the phenylene ring of methylcarbazoles to the other ring. Nevertheless, the signs of the ρ_R coefficients for $\Delta\delta C_{(6)}$ and $\Delta\delta C_{(7)}$ are identical, which makes it possible to speak of a certain amount of transmission of the effects of the substituents from the 3 position of carbazoles also through the biphenyl bond, since the sign of ρ_R changes to negative in benzene on passing from the correlation of $\Delta\delta C_p$ to the correlation of $\Delta\delta C_m$ [15]. In addition, the ranges of the changes in the chemical shifts of the $C_{(6)}$ and $C_{(7)}$ atoms are comparable to one another (2.31 and 2.05 ppm), whereas in benzenes the changes in the chemical shifts of the C_p atoms under the influence of substituents are considerably greater than for the C_m atoms [2, 5, 15].

The fact that the resonance contributions (ρ_R) of the effects of substituents X on $\Delta\delta C_{(9a)}$, $\Delta\delta C_{(6)}$, and $\Delta\delta C_{(7)}$ decrease regularly, whereas the inductive components for the more remote $C_{(6)}$ and $C_{(7)}$ atoms are greater by a factor of approximately two than for the $C_{(9a)}$ atom [Eqs. (3), (6), and (10)], is surprising. The latter fact is difficult to explain within the framework of mechanisms that take into account the σ-inductive effect and the field effect. It must be assumed that the inductive effects of substituents X through the carbazole ring are transmitted primarily via π-inductive effects, which, in turn, indicate high polarizability of the π-electron system of the carbazole fragment.

In addition to their independent interest for the chemistry of heterocyclic compounds, the data obtained on the transmission properties of methylcarbazoles Ia-f are also important for a correct understanding of the nature of the "bridge effect," since it was recently shown [16] in a quantitative evaluation of the effects of substituents on the reactivities of 3-substituted aminocarbazoles that the conductive properties of the carbazole molecule are less pronounced than those of nonplanar diphenylamines. In this connection a comparison of the transmission characteristics of carbazole and diphenylamine in the ground electronic state seems of great interest. We do not have data on the ^{13}C NMR spectra of substituted diphenylamines at our disposal, but published results on the effect of substituents on the ^{19}F NMR chemical shifts in 4'-substituted 4-fluorodiphenylamines are available [17]. Taking into account the fact that the dependence $0.74\ \Delta\delta^{19}F = \Delta\delta^{13}C_p + 0.5$ [1], which is close to linear, exists between δ^{19}F NMR in p-substituted fluorobenzenes and $\delta^{13}C_p$ NMR in substituted benzenes, it is permissible to transform the correlation data for the ^{19}F NMR spectra of substituted fluorodiphenylamines [17] to the ^{13}C NMR scale; in this case we obtain the equation $\Delta\delta C_{4'} = 5.35\sigma_I + 7.67\sigma_R^{\circ}$. A comparison of the latter equation with Eq. (6) shows an approximately twofold increase in the ρ_I and ρ_R coefficients for diphenylamines as compared with methylcarbazoles. Such significant differences in the ρ values, even with allowance for the rough approximation of the equation presented above, constitute evidence that the transmission properties of the planar carbazole ring are lower even in the ground electronic state than in the nonplanar diphenylamine molecule. This unusual fact was explained in [16] by assuming that the carbazole nitrogen atom, as a result of delocalization of the p electrons over the aromatic system, is electron-deficient as compared with diphenylamine. The correctness of this assumption can be verified by comparison of the spectral data for methylcarbazoles Ia-f with the data for the corresponding 3-substituted 9-alkenylcarbazoles, in which, as a result of p,π conjugation, the nitrogen atom becomes even more electron-deficient [3]. Qualitatively speaking, the correlations of $\Delta\delta C_{(6)}$ and $\Delta\delta C_{(7)}$ with the constants of substituents X in 3-substituted 9-vinylcarbazoles have the same character as in the case of methylcarbazoles Ia-f, but the conductivity of the carbazole ring is not only diminished but is even somewhat higher (Table 2). Thus the true reason for the decrease in the transmission properties of the planar carbazole molecule is still not fully explained. For a better understanding of it one needs a direct study of the ^{13}C NMR spectra of substituted diphenylamines in order to compare the electronic conductivity of the latter within the limits of the substituted phenylene ring with the corresponding data for carbazoles.

The effects of the nonadditive influence of substituents on the ^{13}C NMR values in the spectra of benzenes [12, 15] and methylcarbazoles make it possible to assume that diphenylamine (as well as other bridged aromatic and heterocyclic compounds) should not be an exception in this respect. The probable conclusion that the reasons for the nonadditivity effects and the "bridge effect" have general character follows from this.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded in ampuls with a diameter of 10 mm with a Brucker WP-200SY spectrometer (40.32 MHz); the reproducibility was no less than 0.05 ppm. The ^{1}H NMR spectra were recorded with a BS-487C spectrometer (80 MHz).

The methylcarbazoles were synthesized by known methods.

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1,4-DIHYDROPYRIDINE-3,5-DI- AND 2-METHYL-4-ARYL-5-OXO-4,5-DIHYDRO-1H-INDENO[1,2-b]PYRIDINE-3-CARBOTHIONIC ACID ETHYL ESTERS

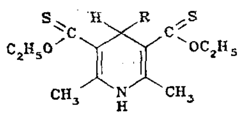
B. A. Vigante, Ya. Ya. Ozols,
G. Ya. Dubur, E. M. Belash,
and Yu. I. Beilis

UDC 547.825'836.3.07:542.943:541.127.1:543.422

Methods for the synthesis of 1,4-dihydropyridine-3,5-di- and 4-aryl-5-oxo-4,5-dihydro-1H-indeno[1,2-b]pyridine-3-carbothionic acid ethyl esters were developed. A comparative analysis of the physicochemical characteristics of this series of substances is given. Their reactivities in electrochemical and chemical oxidation reactions were studied. The electrochemical oxidation potentials of the thionic acid esters are found in a lower anodic range as compared with their oxygen analogs. According to the ionization constants, the thionic acid esters of 4,5-dihydroindenopyridines are stronger acids than the carbonyl esters; this is explained by participation of the free 3d orbitals of the sulfur atom in stabilization of the anion.

Highly effective coronary dilators [1, 2] and hypotensive agents [3] have been found among 4-aryl- and 4-hetaryl-1,4-dihydropyridines (1,4-DHP). 1-Unsubstituted 1,4-DHP are of practical interest as potential antioxidants [4].

Our previous communications [5, 6] were devoted to the results of a study of mono- and polycyclic 1,4-DHP with (alkylthio)carbonyl substituents in the β positions. In the present research we studied the effect of an ethoxythiocarbonyl substituent as compared with an ethoxycarbonyl substituent on the properties of 1,4-DHP (acidities and behavior in electrochemical and chemical oxidation).



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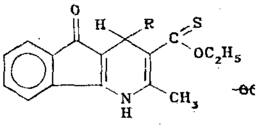

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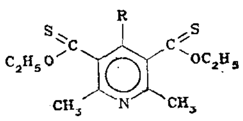

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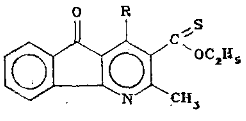

IV

4-Unsubstituted thionic ester I (R = H) is obtained by condensation of acetothioacetic O-ethyl ester (V) with urotropin.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Kharkov Institute of Public Nutrition, Kharkov 310051. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 210-216, February, 1984. Original article submitted June 7, 1983.