# $^{13}C$ NMR SPECTRA OF N-SUBSTITUTED CARBAZOLES. TRANSMISSION OF THE ELECTRONIC EFFECTS OF SUBSTITUENTS THROUGH THE NITROGEN ATOM TO THE CARBAZOLE RING

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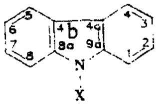
The effect of substituents attached to the nitrogen atom on the $^{13}C$ NMR chemical shifts was determined for a series of 9-substituted carbazoles. Correlation relationships between the inductive and resonance constants of the substituents and the chemical shifts of the carbon atoms were obtained. It was shown that carbazole derivatives are similar to anilines with respect to the conductivity of electronic effects through the nitrogen atom to the carbazole ring.

In [1], by means of $^{13}C$ NMR spectroscopy, we estimated the degree of transmission of electronic effects of substituents from one phenylene ring of 3-substituted 9-methylcarbazoles to the other; it was found that the nature of the substituents in the 3 position has virtually no effect on the chemical shifts (CS) of the methyl groups in the $^{13}C$ NMR spectra. In the present research, we attempted to determine if the effects of substituents are transmitted through the nitrogen atom to the carbazole ring and, if so, the way in which this occurs.

The $^{13}C$ NMR spectra of 9-substituted carbazoles Ia-m with substituents that differ with respect to their electronic and steric characteristics were recorded.



Ia-m

Ia $X=H$; b $X=CH_3$; c $X=C_2H_5$; d $X=p\text{-}C_3H_7$; e $X=iso\text{-}C_3H_7$; f $X=p\text{-}C_4H_9$; g $X=iso\text{-}C_4H_9$; h $X=p\text{-}C_5H_{11}$; i $X=CH_2OH$; j $X=C_6H_5$; k $X=HCO$; *l* $X=COCH_3$; m $X=COCF_3$

The NMR spectra of 10% solutions of Ia-m in $CDCl_3$ were recorded. The assignment of the signals was made on the basis of known data on the $^{13}C$ NMR spectra of carbazoles [2].

An analysis of the data obtained (Table 1) shows that varying substituents X gives rise to an appreciable change in the chemical shifts of the $C_{(3)}$ atoms (the range of change in the chemical shifts of the methyl groups in 3-substituted 9-methylcarbazoles is only 0.8 ppm [1], i.e., transmission of the effect of the substituents from the 3 position through the nitrogen atom formally does not occur, but reverse transmission of the substituent effects is extremely appreciable. In addition to the $C_{(3)}$ position (the para position relative to the nitrogen atom), substituents X have the strongest effect on the chemical shifts of the $C_{(1)}$ atoms (the range of changes is 8.0 ppm) and $C_{(4a)}$ atoms (4.7 ppm), which are in ortho positions relative to the nitrogen atom. Minimal changes in the chemical shifts are observed for the $C_{(2)}$ (2.2 ppm) and $C_{(4)}$ (0.6 ppm) atoms — the meta positions — and for the $C_{(9a)}$ atoms (3.3 ppm). In these respects, the changes in the chemical shifts of the carbon atoms in carbazoles Ia-m are subject to the same principles as in monosubstituted benzenes. Substituents have the strongest effect on the $\delta_{C_o}$ and $\delta_{C_p}$ values of the atoms but not on the $\delta_{C_m}$ values [3].

To evaluate mechanisms for the transmission of the effects of substituents X to the carbazole ring it is important to compare the character of the changes in the chemical shifts of atoms of the same type, viz., $C_{(1)}$ and $C_{(4a)}$ and $C_{(2)}$ and $C_{(4)}$. It follows from Fig. 1

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TABLE 1. C NMR Chemical Shifts (δ, ppm) of N-Substituted Carbazoles Ia-m in $CDCl_3$

| Compound | $C_{(1)}$ $(C_{(8)})$ | $C_{(2)}$ $(C_{(7)})$ | $C_{(3)}$ $(C_{(6)})$ | $C_{(4)}$ $(C_{(5)})$ | $C_{(9a)}$ $(C_{(8a)})$ | $C_{(4a)}$ $(C_{(4b)})$ |
|---|---|---|---|---|---|---|
| Ia | 110,49 | 124,98 | 118,18 | 119,53 | 139,55 | 123,28 |
| Ib | 108,10 | 125,21 | 118,33 | 119,68 | 140,37 | 122,07 |
| Ic | 108,25 | 125,44 | 118,56 | 120,06 | 139,55 | 122,45 |
| Id | 108,32 | 125,21 | 118,26 | 119,68 | 139,92 | 122,07 |
| Ie | 109,89 | 125,29 | 118,49 | 120,13 | 139,25 | 123,04 |
| If | 108,40 | 125,40 | 118,41 | 119,83 | 139,99 | 122,22 |
| Ig | 108,63 | 125,51 | 118,56 | 120,06 | 140,22 | 122,52 |
| Ih | 108,43 | 125,38 | 118,47 | 119,80 | 139,89 | 122,10 |
| Ii | 109,07 | 125,21 | 119,01 | 119,53 | 139,39 | 122,44 |
| Ij | 109,45 | 125,73 | 119,68 | 119,90 | 140,34 | 122,82 |
| Ik | 116,47 | 127,15 | 124,24 | 120,06 | 137,09 | 125,73 |
| Il | 116,02 | 127,15 | 123,49 | 119,68 | 138,35 | 126,10 |
| Im | 116,09 | 125,36 | 127,67 | 119,83 | 137,38 | 126,77 |

TABLE 2. Parameters of Regression Equations $\Delta\delta_{C_i} = a + \rho\sigma$ and $\Delta\delta_{C_i} = a + \rho_I\sigma_I + \rho_R\sigma_R^\circ$ $(\Delta\delta_{C_i} = \delta_{C_i}X - \delta_C H)$ of N-Substituted Carbazoles Ia-m

| Compound | $C_{(i)}$ | Constant | $a$ | $\rho$ | $\rho_I$ | $\rho_R$ | $r$ | $s$ |
|---|---|---|---|---|---|---|---|---|
| 1 | $C_{(1)}$ | $\sigma_p$ | −0,67 | 10,21 | | | 0,933 | 1,48 |
| 2 | $C_{(1)}$ | $\sigma_p{}^+$ | −0,12 | 7,61 | | | 0,965 | 0,95 |
| 3 | $C_{(1)}$ | $\sigma_m{}^\circ$ | −0,88 | 13,27 | | | 0,937 | 1,44 |
| 4 | $C_{(1)}$ | $\sigma_R{}^\circ$ | 0,33 | 19,58 | | | 0,969 | 1,01 |
| 5 | $C_{(1)}$ | $\sigma_I, \sigma_R{}^\circ$ | 0,57 | | 2,95 | 22,06 | 0,9716 | 1,09 |
| 6 | $C_{(4a)}$ | $\sigma_p$ | −0,42 | 5,53 | | | 0,972 | 0,50 |
| 7 | $C_{(4a)}$ | $\sigma_p{}^+$ | −0,04 | 4,31 | | | 0,973 | 0,51 |
| 8 | $C_{(4a)}$ | $\sigma_m$ | −0,52 | 7,13 | | | 0,970 | 0,52 |
| 9 | $C_{(4a)}$ | $\sigma_I, \sigma_R{}^\circ$ | 0,84 | | 1,24 | 9,16 | 0,9743 | 0,54 |
| 10 | $C_{(2)}$ | $\sigma_p$ | 0,39 | 3,67 | | | 0,964 | 0,29 |
| 11 | $C_{(2)}$ | $\sigma_p{}^+$ | 0,64 | 2,16 | | | 0.822 | 0,58 |
| 12 | $C_{(2)}$ | $\sigma_m$ | 0,32 | 4,77 | | | 0,971 | 0,25 |
| 13 | $C_{(2)}$ | $\sigma_I$ | 0,19 | 8,21 | | | 0,926 | 0,42 |
| 14 | $C_{(2)}$ | $\sigma_I, \sigma_R{}^\circ$ | 0,36 | | 5,68 | 2,06 | 0,9433 | 0,43 |
| 15 | $C_{(3)}$ | $\sigma_p$ | 0,84 | 10,51 | | | 0,989 | 0,58 |
| 16 | $C_{(3)}$ | $\sigma_p{}^+$ | 1,65 | 7,86 | | | 0,942 | 1,41 |
| 17 | $C_{(3)}$ | $\sigma_m$ | 0,62 | 13,68 | | | 0,995 | 0,39 |
| 18 | $C_{(3)}$ | $\sigma_I$ | 0,46 | 20,12 | | | 0,974 | 0,90 |
| 19 | $C_{(3)}$ | $\sigma_I, \sigma_R{}^\circ$ | 0,89 | | 13,53 | 7,05 | 0,9884 | 0,68 |

that in the case of great "sensitivity" of the $C_{(1)}$ atoms to the effect of substituents X a good linear relationship with slope $\rho = 0.51$ $(r = 0.987)$ exists between the $C_{(1)}$ and $C_{(4a)}$ chemical shifts. The twofold intensification of the effects of the substituents on the $C_{(1)}$ atom is, in all likelihood, determined primarily by the relative closeness of the $C_{(1)}$ atoms and substituents X and by the effect of the latter on shielding of the $C_{(1)}$ atoms through space. At the same time, one might have expected that, because of their close location, additional effects of steric compression by substituents X would influence the change in the chemical shifts of the $C_{(1)}$ atoms, in contrast to the $C_{(4a)}$ atoms. According to x-ray diffraction data, steric reciprocal influence of substituents X and $C_{(1)}$–X groups is manifested even in the case of 9-methylcarbazole (Ib) [4]. However, there is no relationship whatsoever between the chemical shifts of the $C_{(1)}$ atoms and $E_s$ or other steric constants in the series of 9-alkyl-substituted carbazoles Ib-h, which have substituents that differ relatively markedly with respect to their steric characteristics. The independence of the chemical shifts of the $C_{(1)}$ atoms on the volume of substituents X is evidently the result of a certain constant contribution of steric compression to shielding of these atoms.

We were unable to establish a satisfactory relationship between the changes in the chemical shifts of the $C_{(2)}$ and $C_{(4)}$ atoms (meta position); this is evidently determined by the narrow range of changes in the $\delta_{C(4a)}$ values (0.6 ppm).

We used the relative chemical shifts $\Delta\delta_{C_i} = \delta_{C_i}X - \delta_C H$ for a quantitative evaluation of the effect of substituents in carbazoles Ia-m on the chemical shifts of the carbon atoms (Table 2).

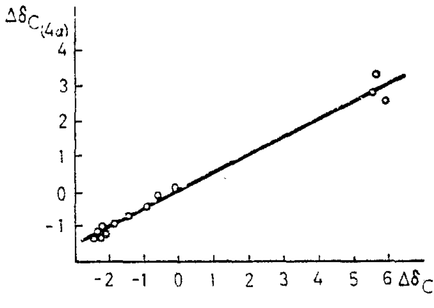


Fig. 1

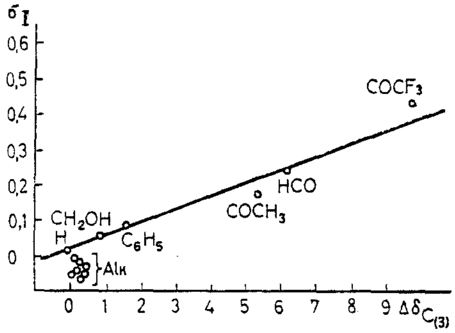


Fig. 2

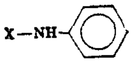
Fig. 1. Interrelationship between the chemical shifts of the $C_{(4a)}$ and $C_{(1)}$ atoms.

Fig. 2. Dependence of the chemical shifts of the $C_{(3)}$ atoms on the inductive constants of the substituents.

The changes in the chemical shifts of the $C_{(1)}$ and $C_{(4a)}$ atoms are described satisfactorily by correlation Eqs. (1)-(9) (Table 2); correlation relationships of the best quality are obtained when the $\sigma_R°$ constants are used for the $\Delta\delta_{C(1)}$ values and the $\Delta\sigma_p^+$ constants are used for the $\Delta\delta_{C(4a)}$ values [Eqs. (4) and (7), respectively], and this constitutes a significant difference between carbazoles and monosubstituted benzenes, for which simple linear dependences of the chemical shifts of the $C_o$ atoms on the electronic effects of substituents are not observed [5].

Because of the narrow range of the change in the chemical shifts of the $C_{(4)}$ atoms, it is impossible to statistically reliably evaluate the quantitative influence of the electronic effects of substituents X on them. At the same time, the $\Delta\delta_{C(2)}$ values change in a regular manner under the influence of substituents X [Eqs. (10)-(14)]; correlation relationships of the best quality were obtained when the $\sigma_m$ constants of substituents X were used in this case. It would seem that there is nothing unusual in this, since the $C_{(2)}$ atoms are meta-oriented relative to the nitrogen atom of carbazoles Ia-m. However, the best dependences of the $\Delta\delta_{C(3)}$ values (para position) are also observed for the $\sigma_m$ and $\sigma_I$ constants of substituents X [Eqs. (17) and (18)]. At the same time, it is known that the changes in the chemical shifts of the $C_p$ atoms in monosubstituted benzenes are described most satisfactorily by means of the $\sigma_p^+$ constants of the substituents [2]. A natural question arises — is the dependence of the $\Delta\delta_{C(3)}$ values on the inductive effects of the substituents determined only by the specific characteristics of the heterocyclic structure of carbazoles? The result obtained formally indicates that the nitrogen atom in carbazole isolates the ring from the effect of direct polar conjugation of substituents X.

N-Substituted anilines may be noncyclic analogues of carbazoles Ia-m.



IIa-f

II a X=H; b X=CH₃; c X=NH₂; d X=C₆H₅; e X=COCH₃, f X=C₂H₅

An analysis of the literature data from the $^{13}C$ NMR spectra of N-substituted anilines IIa-f shows that the effect of substituents on the change in the chemical shifts of the $C_p$ atoms is also determined by the inductive properties of substituents X [the compound number and the $\delta C_p$ value (ppm) are given]: IIa 118.35 [6]; IIb 117.07 [6]; IIc 119.15 [6]; IIe 123.10 [7]; IId 120.91 [6]; IIf 117.12 [6]; $\rho = 19.95$; $r = 0.956$. However, this does not mean that only the inductive effects of substituents X are transmitted through the nitrogen atom in anilines IIa-f. The dependence presented for anilines is part of a general principle for anilines $X_2NC_6H_5$ that shows that there is a linear interrelationship between the $\sigma_I$ constants of the X groups and the $\sigma_R°$ constants of the $X_2N$ fragments [6]. Taking into account the fact that, for example, completely distinct mesomeric reciprocal influences of the carbon atoms of the carbazole ring and the C=C bond are observed in the $^{13}C$ NMR spectra of 9-alkenylcarbazoles [8, 9], one can completely validly assume that the relationships between the $\Delta\delta_{C(3)}$ values and the $\sigma_I$ constants found in the case of carbazoles Ia-m are also the result of symbatic changes in the inductive constants of substituents X and the resonance effects of the

$>N-X$ fragments. From this point of view, carbazoles Ia-m do not differ qualitatively from anilines. However, the fundamental difference in the effect of radicals X on the change in the chemical shifts of the $C_{(3)}$ atoms in carbazoles Ia-m and N-substituted anilines is manifested in the fact that alkyl substituents, which are weak electron donors when they are attached to the nitrogen atom, nevertheless give rise to deshielding of the $C_{(3)}$ atoms in the $^{13}C$ NMR spectra (Table 1). Figure 2 graphically shows that the points for alkylcarbazoles Ib-h, but not the point for carbazole (Ia), deviate from the general regression line. This deshielding of the $C_{(3)}$ atoms, which are free from steric effects, under the influence of alkyl groups is also not in agreement with nonempirical quantum-chemical calculations, which show that the increase in the electron density on the $C_{(3)}$ atom of 9-methylcarbazole (Ib) is comparable to that observed for carbazole (Ia) [10].

It is important to note that the order of the increase in the shielding of the tertiary carbon atoms of the carbazole rings, viz., $\delta C_{(2)} < \delta C_{(4)} < \delta C_{(3)} < \delta C_{(1)}$, which coincides with the order of the increase in the electron densities on these atoms in carbazole (Ia) [11], is disrupted for carbazole Im, which has a strong electron-acceptor $COCF_3$ substituent. In this case, the $C_{(1)}$ and $C_{(4)}$ atoms prove to be more shielded than the $C_{(2)}$ and $C_{(3)}$ atoms: $\delta C_{(3)} < \delta C_{(2)} < \delta C_{(4)} < \delta C_{(1)}$. This provides a basis for the assumption that the regiospecificity of attack by the electrophile may change from the usually observed 1 and 3 positions of carbazole in electrophilic substitution reactions of 9-X-carbazoles with strong electron-acceptor substituents. This conclusion is also confirmed by the results obtained in [12], in which it was shown that 2,7-dinitro-9-trifluoroacetylcarbazole is formed in the nitration of carbazole Im.

It has been previously established [13, 14] that a rectilinear dependence of the ionization potentials on the inductive constants of substituents in the 9 position of the carbazole molecule exists. The observed dependence of the chemical shifts of the $C_{(3)}$ atoms in N-substituted carbazole on the inductive constants of the substituents, together with the data in [13, 14], can be used for the qualitative evaluation of the ionization potentials from the chemical shifts of the carbon atoms.

## EXPERIMENTAL

The $^{13}C$ NMR spectra were recorded with a BS-567A spectrometer (25.142 MHz) and ampuls with a diameter of 10 mm; the reproducibility was no less than 0.05 ppm. The chemical shifts were measured relative to the central peak of the signal of $CDCl_3$ (76.9 ppm).

Carbazoles Ia-m were synthesized by known methods.

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