had mp 162-163°C (from isopropyl alcohol). Found: Cl 11.1%. C17H14N4·HCl. Calculated: Cl 11.3%.

LITERATURE CITED


ACIDITIES OF 1-INDOLYLACETIC AND CARBAZOLYLACETIC ACIDS.

INDUCTIVE CONSTANTS OF INDOLY AND CARBAZOLYL GROUPS

V. D. Filimonov M. M. Sukhoroslova, V. T. Novikov, and T. V. Vidyagina

The pKₐ values of 1-indolylacetic, 3-(9-ethyl)carbazolylacetic, and a number of
3,6-disubstituted 9-carbazolylacetic acids in aqueous ethanol solutions were
determined by potentiometry. The inductive constants of the corresponding
heterocyclic fragments were calculated from the values obtained. It is shown
that annelation of the benzene ring with the pyrrole ring of indole gives rise
to a decrease in the negative inductive effect of the heteroring. A linear re-
relationship between the acidic properties of carbazoles and the corresponding
9-carbazolylactic acids was established.

We have previously shown [1, 2] that the terminal sp²-hybridized atom in the 9-alkenyl-
carbazole series is appreciably less shielded in the ¹³C NMR spectra as compared with N-vinyl
derivatives of pyrrole [3]. This fact indicates the smaller effect of p-π conjugation of
the p electrons of the nitrogen atom of the carbazolyl ring with the π electrons of the C=C
bond. However, the possibility that deshielding of the terminal vinyl atom on passing from
1-vinylpyrrole (chemical shift 95.89 ppm [4]) and 1-vinylindole (96.0 ppm [5]) to 9-vinyl-
carbazole (101.18 ppm [1]) may be determined by (in addition to steric reasons) an increase
in the negative inductive effect of the heteroring in the same order is not excluded;
whereas in ordinary enamines the effects of conjugation prevail over the negative inductive
effects of the aminoalkyl or aminocycloalkyl groups [6], in the N-vinylamines under dis-
cussion, in addition to p-π conjugation, one observes the competitive and conjugation-
weakening delocalization of the p electrons in the heterocyclic fragments, which may appreci-
ably increase the role of inductive effects in the distribution of the electron densities
of the C=C groups and their contribution to the reactivity. It is only natural that quan-
titative data on the σI constants of the indicated heterocycles not only are necessary for
a solution of the problem noted above but are also of fundamental importance for an under-
standing of the chemistry of heterocycles of the pyrrole series.

In the present research to determine the inductive constants of 1-indolyl and carbazolyl
groups we determined the pKₐ values in aqueous ethanol of a number of acetic acids that
contain a heterocyclic fragment, viz., 1-indolylactic (I), 9-carbazolylacetic (IIa-e), and
3-(9-ethylcarbazolyl)acetic (III) acids.

S. M. Kirov Tomsk Polytechnic Institute, Tomsk 634004. Translated from Khimiya
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The method for the determination of the inductive constants of various groups from the pK\textsubscript{a} values of substituted acetic acids is well known, and, of particular importance in our case, steric factors do not have an appreciable effect on the \( \sigma_I \) constants obtained [7].

The thermodynamic pK\textsubscript{a} values of acids I-III (Table I) were determined by potentiometry [8] at 25 \( \pm \) 0.5°C. The pK\textsubscript{a} values found for acids IIa-e in 50 and 60% aqueous ethanol are linearly related to the \( \sigma^o \) constants of the X and Y substituents [Eqs. (1) and (2), respectively]:

\[
pK_a = 4.63 - 0.38\sigma^o; \quad S = 0.02; \quad r = 0.990
\]

\[
pK_a = 4.92 - 0.54\sigma^o; \quad S = 0.03; \quad r = 0.985
\]

where \( \rho \) is the reaction constant, \( S \) is the standard deviation, and \( r \) is the correlation coefficient. The decrease in the \( \rho \) value as the fraction of ethanol in solution decreases for acids II is a characteristic feature also for substituted phenylacetic acids: the \( \rho \) values in 75, 50, and 10% aqueous ethanol are, respectively, 0.83, 0.71, and 0.54 [9]. A comparison of the \( \rho \) values for acids IIa-e and phenylacetic acids in 50% ethanol indicates appreciably lower sensitivity of the dissociation constants of 9-carbazolylacetic acids to the effect of the substituents, i.e., the less pronounced transmission properties of the carbazolyl ring as compared with the phenyl group. A study of the effect of the composition of the medium on the strength of acid Ia showed that as the fraction of ethanol is increased from 50% to 95%, the acid properties of Ia become weaker; the dependence of the pK\textsubscript{a} on the percentage of ethanol has approximately linear character [Eq. (3)]:

\[
pK_a = 3.43 + 0.025\% \text{EtOH}; \quad S = 0.07; \quad r = 0.980
\]

Measurement of the acidity of acid Ia in more dilute ethanol solutions is not possible because of its limited solubility. The effect of the medium on the strength of acid IIa is similar to its effect on the strength of other aliphatic carboxylic acids [10]. From the pK\textsubscript{a} values of acids I and IIa in a 56% by volume solution of ethanol (mass content 50%) by means of the equation in [11]

\[
\sigma^* = 8.18 - 1.13pK_a
\]

we calculated the Taft inductive constants for the 9-carbazolyl (\( \sigma^* = 1.55 \pm 0.05 \)) and 1-indolyl (\( \sigma^* = 1.75 \pm 0.05 \)) groups. We also calculated the \( \sigma_I \) constants from the expression \( \sigma_I = \sigma^*/6.23 \): 0.25 \( \pm \) 0.01 (9-carbazolyl) and 0.28 \( \pm \) 0.01 (1-indolyl). It is interesting to note that extrapolation of the dissociation constant of acid IIa to a purely aqueous solution by means of Eq. (3) (although such extrapolation is not theoretically substantiated) gives a pK\textsubscript{a} value of 3.43. The use of the Charton correlation relationship between the pK\textsubscript{a} values and the \( \sigma_I \) constants for aqueous solutions of substituted acetic acids at 25°C, viz., \( \sigma_I = 1.186 - 0.25 \text{pK}_a \) [7], leads to a \( \sigma_I \) constant of 0.32 for the 9-carbazolyl group. This does not differ much from the \( \sigma_I \) value of 0.25 obtained from Eq. (4), and this to a certain extent confirms the correctness of the constant for the 9-carbazolyl group. However, the chief significance of the pK\textsubscript{a} value obtained by extrapolation consists in the fact that it makes it possible to make an approximate comparison of the strength of acid IIa with the strengths of other carboxylic acids, the acidities of which in very many cases have been determined in aqueous solutions.

The effect of the substituents in the carbazolyl ring on the strengths of acids IIa-e coincides qualitatively with the effect of the same substituents on the NH acidities of carbazoles in DMSO [12]. (The pK\textsubscript{a} values of 3-methylcarbazole, carbazole, 3-nitrocarbazole, and 3,6-dichlorocarbazole are, respectively, 17.29, 16.55, 14.10, and 15.23.) An approximate linear relationship exists between the pK\textsubscript{a} values of acids IIa, d, e (in 60% ethanol) and 3-methyl-9-carbazolylacetic acid, the pK\textsubscript{a} of which was calculated from Eq. (2), and the pK\textsubscript{a} values of the carbazoles indicated above [Eq. (5)]:

\[
pK_{a\text{acid}} = 1.98 + 0.17pK_a\text{carbazole}; \quad S = 0.22; \quad r = 0.984
\]