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APPLICATION OF THE HAMMETT - STREITWIESER EQUATION TO INTERPRETATION OF THE CHEMICAL SHIFTS OF NONAROMATIC PROTONS IN SUBSTITUTED ARENES

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The chemical shifts of the methyl group of methylarenes have recently been interpreted in terms of diamegnetic shielding by aromatic ring currents[1)] or in terms of hyperconjugation[2)]. The later interpretation was also given[2)] for a series of arylmethylbromides and arylmethylcarbinols.

The purpose of this paper is to describe the application of the Hammett-Streitwieser equation[3),4)] to the correlation of the position constants with the chemical shifts of side-chain protons in a series of substituted arenes. The main idea of this method is very similar to that of the Hammett equation[5)], however the Hammett substituent constants σ are replaced by position constants σ_r defined as follows[6)]:

$$\sigma_r = \lg K_r - \lg K_{\alpha\text{-naphth.}} \qquad (1)$$

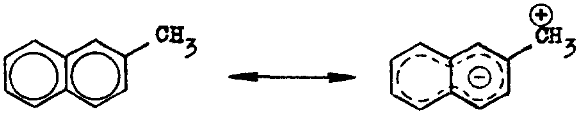
where K_r and $K_{\alpha\text{-naphth.}}$ are the acid-base equilibrium constants of the r-th position of a given arene and of the alpha-position of naphthalene, respectively. These position constants were originally used by Streitwieser[6)] to interpret the reaction rates of the nitration, chlorination, and deuteroprotonation of arenes. Recently, in a series of papers[3),4)], the application of these constants to the interpretation of not only purely chemical but also various physical properties of arenes and their monosubstituted derivatives has been demonstrated. For arenes linear relationships between position constants and[3)]: proton chemical shifts, ionization potentials, polarographic half-waves for oxidation and for reduction, location of the para-band in UV-spectra, electron affinities and the location of the CT-bands with various electron acceptors$^{7)}$, and the HMO -calculated values of $E_{LEMO} = -E_{HOMO}$ have been found. In the case of monosubstituted derivatives of arenes, for a constant functional group Y the following correlations have been found$^{4)}$: for polarographic half-wave potentials of oxidation of amines, for pK-values of these amines, for UV-spectral data of arylbenzophenones, for polarographic half-wave potentials of reduction of nitroarenes$^{8)}$, quinones$^{9)}$, and diarylketones$^{9)}$. In all these cases the correlation coefficients were about 0.95 or better, usually near to 0.99.

For the properties depending on the position of the functional group, the Hammett-Streitwieser equation has a form:

$$Q_r = Q_o + \sigma_r \rho \tag{2}$$

where Q_r is the numerical value of the property, Q_o is the intercept, and ρ is the slope of the linear regresion, having a physical meaning similar to that of the original Hammett equation, namely the measure of the sensitivity of the process under consideration to structural effects.

Application of the Hammett-Streitwieser equation in form (2) to the title problem results from the following consideration. The position constants σ_r are, from the quantum-chemical point of view, simply related$^{6)}$ to the Wheland$^{10)}$ localization energy L_r^+. However this quantity, for the benzenoid hydrocarbons, has the same magnitude in the case when the rest of the molecule is negatively charged$^{6)}$. Thus the position constants in such a model describe the tendency of the residual molecule to delocalize the insufficiency or the excess of the charge. The position constants describe the ability of the residual molecule to attract the pseudo-pi electrons from, for example, the methyl group in the case of methylaryl systems. In such a manner the position constants should describe the changes of charge density on methyl group in dependency on the aryl-skeleton to which this group is attached in position r. Schematicaly it can be drawn as follows:



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and the contribution of V.B. structure II should depend distinctly on the position constant σ_r. In fact, a good correlations (Fig. 1.) are obtained relating the chemical shifts of nonaromatic protons of methylarenes, arylmethylbromides, arylmethylcarbinols, and aminoarenes to the appropriate position constants.

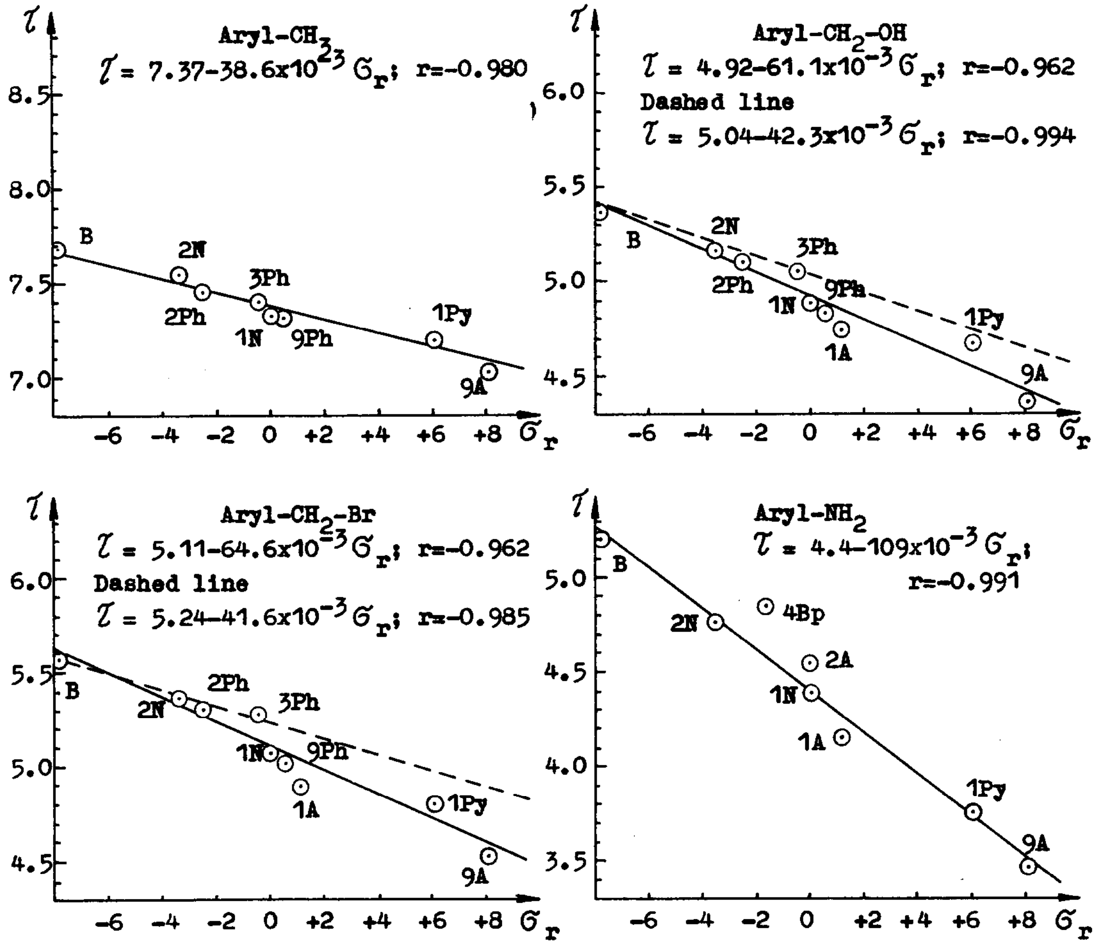

Fig.1.Correlations of the position constants σ_r to the chemical shifts in τ units of nonaromatic protons in substituted arenes. Dashed lines - correlations when points of arenes substituted in positions of classes 1 and 2 are excluded. Abbreviations: derivatives of benzene = B, naphthalene = N, phenanthrene = Ph, anthracene = A, pyrene = Py, biphenyl = Bp, numbers denote the position. σ_r values were taken from [6] or [3], chemical shifts data were taken: for methylarenes, arylmethylbromides, and arylmethylcarbinols from [2], for aminoarenes from [12].

The best correlation coefficient is found for methylarenes. However it should be pointed out, that almost the same values of correlation and regression coefficients are obtained for the Aryl-CH_2-X series if the molecules with the substituent in 1- and 9-anthracyl-type positions (positions of classes 1 and 2 according to the classification due to Koutecký et al.[11]) are excluded.

It should be noted that all excluded points are deviated deviate downfield of the correlation lines (dashed), whereas the deviations in Bentley and Dewar's correlations[2] are irregular. The systematic character of the deviations in our correlations for Aryl-CH_2-X suggests ~~the~~ a steric origin ~~of~~ for these because all aberrant points belong to the molecules in which steric interactions are possible.

The greater value of ρ for the regression line of aminoarenes than for the other series of compounds show that the chemical shifts of amino-protons are more sensitive to structural effects than the chemical shifts of protons of methyl or methylene groups.

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