THE REACTIVITY OF 6,9-DICHLORACRIDINES DERIVATED

Maltseva T.I., Kolisnyk O.V.
The National University of Pharmacy, Kharkiv, Ukraine
elenfarm@mail.ru

Substituents of 9-chloracridine are widely used as starting substances for obtaining various biologically active 9-amino-, 9-alkylamino-, 9-arylamino-, 9-hydrazineacridines; markers in genetic engineering; luminescent indicators in analytical chemistry.

The aim of the research is to study of reactivity of substituted 6,9-dichloracridines because the reactivity of compounds of this homologous series has not been investigated in details.

The constants of ionization pK_{BH}^{+} of substituted 6,9-dichloracridines have been determined in the mixed ethanol-water solvent (50 mole percent of ethanol) at the temperature of 25^0C by the method of potentiometric titration. It has been shown that these compounds are weak bases (pK_{BH}^{+} of the corresponding associated acids is in the range of 3.71-3.95). It has been proven that their basicity depends upon the nature and position of substituents in the heterocycle. Introduction of 9-chlorine substituent to the molecule of acridine leads to significant weakening of basic properties (pK_{sub}^{+} = 0.82) due to decrease of electron density on the atom of nitrogen (reactive centre). The appearance of 9-chloracridine of chlorine atoms in the molecule in 2-, 4-positions also decreases basicity of the heterocycle, but approximately 6.5 times less (pK_{sub}^{+} = 0.13 (2-Cl), pK_{sub}^{+}= 0.14 (4-Cl)). On the contrary, the donor substituents increase basicity. The quantitative assessment of the substituents influence has been performed within the principle of available energy linearity according to the Hammet equation by the correlation analysis method. The equation obtained, which includes pK_{BH}^{+} of all experimental compounds, proved to be statistically uncertain. On the plot of pK_{BH}^{+}- f(σ) dependence, the value of pK_{BH}^{+} for 4-methoxy substituent is supposed to be out of the linear dependence. Elimination from correlation of pK_{BH}^{+} for 4-methoxy substituted 6,9-dichloracridine allowed to obtain the correlation equation of pK_{BH}^{+}- f(σ) relationship with reliable statistic characteristics. This equation allows to predict reactivity of other members of this homologous series. The low value of the reaction constant is ρ = 0.86 and testifies a slight sensitivity of the reactive centre (heterocyclic atom of nitrogen) to the influence of substituents in the molecule of substituted 6,9-dichloracridine. It is notable that the reactive constants ρ for 6,9-dichloracridines, 5-nitro-9-chloracridines within the limits of experimental error coincide, and it indicates the single mechanism of the electronic influence of substituents on the reactive centre.