Cooling of the aqueous filtrate yielded 0.3 g (30%) of 3-phenylthiocarbamoylthiazolidine-2,4-dione VI with mp 155-156°. Found: C 47.8; H 3.2; N 10.8%; M 229 (in mass-spectrum). C₁₀H₁₀N₂O₂S₂. Calculated: C 47.6; H 3.2; N 11.1%; M 232. Evaporation of the hydrochloric acid filtrate gave 0.38 g (38%) of 3-phenylthiazolidine-2,4-dione III with mp 142-143° (no melting-point depression was observed for a mixture of this product with the product obtained by the method in [3]). The hydrochloric acid filtrate was neutralized with 10% Na₂CO₃ solution, saturated with alkali, and extracted with ether. The ether extract was treated with a mixture of acetic acid and acetic anhydride and the mixture was worked up to give acetanilide, with mp 114° (from water), which was identified by a mixed-melting point determination.

LITERATURE CITED

HAMMETT CONSTANTS OF THE PYRROLINE-2,5-DIONE RING

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and S. V. Iksanova

The electronic effect of the pyrroline-2,5-dione ring on the benzene ring in the case of N-aryl compounds is close to the effect exerted by halogens. The overall electron-acceptor effect depends markedly on the nature of the solvent. The electron-donor effect of conjugation is small.

In the present paper we have made a quantitative evaluation of the electronic nature of the pyrroline-2,5-dione (maleimide) and pyrrolidine-2,5-dione rings within the framework of the Hammett-Taft method.

In conformity with this, we determined the σ constants of pyrroline-2,5-dion-1-yl (I), pyrrolidine-2,5-dion-1-yl (II), and 3-chloropyrrolidine-2,5-dion-1-yl (III) substituents for the para (σₚ) and meta (σₘₚ) positions with respect to the ionization of p- and m-substituted benzoic acids and, on the basis of the results, estimated, from the Taft equations, the independent contributions and the magnitudes of the substituent constants of the inductive (σᵢ) and conjugation (σₑ) effects. The σᵢ and σₑ constants found were compared with the corresponding constants calculated on the basis of the F¹H NMR chemical shifts in the spectra of p- and m-substituted fluorobenzenes.

The information obtained may be of interest in connection with the fact that in recent years maleimides have received widespread recognition as subjects for the investigation of the chemistry of heterocyclic chain polymers [1].

The σ constants of substituents I-III in the equation


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were found with respect to the ionization of p- and m-substituted benzoic acids in 50% aqueous ethanol at 25°C. The reaction constant for the indicated conditions was assumed to be 1.535 \cite{2}, and the dissociation constant of unsubstituted benzoic acid was assumed to be 5.71 \cite{3}. The investigated acids are stronger than benzoic acid, and the electron-acceptor properties of the rings of I-III are less expressed when they are in the para position than when they are in the meta position; this is characteristic for substituents that have opposite inductive and conjugation effects. The \( \sigma \) constants of the substituents calculated from Eq. (1) are presented in Table 1 along with the results of separation of the Hammett constants into independent contributions of the inductive and conjugation effects from Taft equations (2) and (3) \cite{4}:

\[
\sigma_i = \frac{1}{\rho_1 (1 - \alpha)} \lg \frac{k_m}{k_p} - \lg \frac{k_p}{k_o},
\]

\[
\sigma_c = \frac{1}{\rho_1} \lg \frac{k_p}{k_o} - \sigma_i,
\]

where \( k_m, k_p, \) and \( k_o \) are, respectively, the ionization constants of m- and p-substituted benzoic acid and unsubstituted benzoic acid, \( \rho_1 \) is the reaction constant for the inductive effect, and \( \alpha \) is a constant that depends on the type of reaction. In our calculations the \( \rho_1 \) and \( \alpha \) values were assumed to be 1.50 and 0.42, respectively \cite{5}.

Considering the high tendency of the oxygen atom of the carbonyl groups of the rings of I-III to form hydrogen bonds with proton-donor solvents, it must be noted that the \( \sigma, \sigma_i, \) and \( \sigma_c \) constants calculated from Eqs. (1)-(3) characterize the investigated substituents in the state of solvation, which, as one might assume, increases their electron-acceptor character due to intensification of the \( \sigma, \pi \)-accepting effect of the carbonyl groups.

In this connection, it seemed of interest to compare the Taft constants calculated from reactivity data with the analogous values calculated on the basis of the \( F^{19} \) NMR chemical shifts in the spectra of m- and p-substituted fluorobenzenes, which, it is well known, quite accurately reflect the effect of a substituent on the electronic system of the benzene ring via an inductive mechanism and the conjugation effect \cite{6}. With this end in mind, we investigated the \( F^{19} \) NMR spectra of m- and p-substituted fluorobenzenes with substituents I-III in dichloroethane solutions and calculated the Taft constants from Eqs. (4) and (5) (Fig. 1 and Table 1):

\[
\delta_m = -7.1 \sigma_i + 0.6,
\]

\[
\delta_p = \delta_m - 29.5 \sigma_c,
\]

where \( \delta_m \) and \( \delta_p \) are the chemical shifts of the fluorine nuclei in m- and p-substituted fluorobenzenes reckoned from the signal of unsubstituted fluorobenzene and expressed in parts per million of the resonance frequency; positive \( \delta \) values indicate an increase in the shielding of the fluorine nuclei.

We also estimated the constants of the pyrroline-2,5-dione ring from the shift of the band of the OH stretching vibrations in the spectrum of 1-(4-hydroxyphenyl)pyrrolidine-2,5-dione relative to the analogous band in the spectrum of unsubstituted phenol in CCl\(_4\) solution. The II and III substituents cannot be similarly investigated because of the low solubility of 1-arylpyrrolidine-2,5-diones in nonpolar organic solvents.

The analysis of the correlation of the \( \sigma \) substituent constants with the shifts of the vibrational frequencies (\( \Delta \nu_{OH} \)) in the spectra of p-substituted phenols carried out in \cite{7} constitutes evidence that the latter fit extremely well on the correlation line \( \sigma = -0.0645 \Delta \nu_{OH} \). This dependence makes it possible to estimate the \( \sigma \) constant of the pyrroline-2,5-dione ring (\( \Delta \nu_{OH} = -3.5 \text{ cm}^{-1} \)) as \( 0.23 \pm 0.03 \) for a confidence probability of 0.95.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>( \eta_{\text{meta}} )</th>
<th>( \delta_{\text{meta}} )</th>
<th>( \eta_{\text{para}} )</th>
<th>( \delta_{\text{para}} )</th>
<th>( \sigma_i )</th>
<th>( \sigma_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrroline-2,5-dione-1-yl</td>
<td>5.21</td>
<td>-0.326</td>
<td>5.30</td>
<td>0.267</td>
<td>+0.494</td>
<td>0.377</td>
</tr>
<tr>
<td>Pyrrolidine-2,5-dione-1-yl</td>
<td>5.19</td>
<td>0.330</td>
<td>-1.55</td>
<td>5.23</td>
<td>0.313</td>
<td>-0.200</td>
</tr>
<tr>
<td>3-Chloropyrrolidine-2,5-dione-1-yl</td>
<td>4.99</td>
<td>0.466</td>
<td>-2.15</td>
<td>5.01</td>
<td>0.456</td>
<td>-1.320</td>
</tr>
</tbody>
</table>

TABLE 1. \( \sigma \) Substituent Constants and \( pK_a \) Values of m- and p-Substituted Benzoic Acids and \( F^{19} \) Chemical Shifts in the Spectra of m- and p-Substituted Chlorobenzenes