Charge Density-$pK_b$ Correlations in Certain Substituted Anilines

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The total $(\pi + \sigma)$ charge densities at the basic nitrogen atom of ten substituted anilines have been calculated by Hückel LCAO MO and Del Re methods. A good correlation (correlation coefficient $= 0.98$) is obtained between the calculated charge densities and experimental $pK_b$ values of these anilines.

Recently quantum mechanical calculations have been made on several homocyclic and heterocyclic aromatic molecules and the data used to explain the preferred position of electrophilic attack and also the observed trend in the experimental activation energies for molecular bromination of these compounds$^{1-3}$. The inclusion of $\sigma$-charges in such correlations was found essential$^4$. In this note, we report the total charge densities on the basic nitrogen atom of ten substituted anilines and their correlation with their $pK_b$ values, in order to render Hammett correlations more quantitative.

$\pi$-Charges were calculated by Hückel LCAO MO method and $\sigma$-charges by Del Re method$^5-13$. Berthod-Pullman parameters which give charge density distributions comparable with those obtained by $ab$ initio method were used in these calculations. The parameters for nitro group in the calculation of $\sigma$-charges being not available were calculated using Del Re equation$^{14}$. The calculations of $\pi$- and $\sigma$-charges were programmed in FORTRAN for the computer IBM 1130. Using these programmes the $\pi$- and $\sigma$-charges at an atom were calculated separately and then added to get the total charge density$^{15,16}$.

The total charge densities ($\Delta Q_j$) on the basic nitrogen atom of ten substituted anilines are given in Table 1, along with their $pK_b$ values. The $\pi$-charge density data indicate that this nitrogen atom becomes positively charged due to delocalisation of the lone pair of electrons. Thus the basicity of anilines is mainly due to the inductive effect of the amino group. In this correlation only para and meta substituted anilines have been included in order to avoid complications due to ortho-effect. It is clear from Table 1 that as the total charge density on the basic nitrogen atom increases, the $pK_b$ value decreases. Further, a linear relationship is obtained between the calculated charge densities and the experimental $pK_b$ values with a correlation coefficient of 0.98, indicating a reasonably good correlation.

Table 1—$\pi$, $\sigma$ and Total Charge Densities at the Basic Nitrogen Atom of Certain Substituted Anilines

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecule</th>
<th>(Charge density) $\times 10^3$</th>
<th>$\Delta Q_\pi$</th>
<th>$\Delta Q_\sigma$</th>
<th>$\Delta Q_t$</th>
<th>$pK_b$</th>
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<td>1</td>
<td>$p$-Nitroaniline</td>
<td>$196$</td>
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<td>$-354$</td>
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<td>2</td>
<td>$m$-Nitroaniline</td>
<td>$132$</td>
<td>$-546$</td>
<td>$-414$</td>
<td>$11.5$</td>
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</tr>
<tr>
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<td>$m$-Chloroaniline</td>
<td>$108$</td>
<td>$-570$</td>
<td>$-462$</td>
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<tr>
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<td>$087$</td>
<td>$-572$</td>
<td>$-485$</td>
<td>$10.2$</td>
<td></td>
</tr>
<tr>
<td>5</td>
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<td>$-565$</td>
<td>$-475$</td>
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<tr>
<td>6</td>
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References