Interaction between Two Molecules of Pyridine in Ground State

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Using free electron model for the π-electron system in pyridine, the interaction energy is expanded in terms of the small overlap \( S_{12} \) and analytical energy expressions are obtained in terms of \( S_{12} \) between a pair of molecules situated parallelly with reference to the axes of the molecules in the ground state.

The force of interaction between a pair of conjugated molecules plays an important role in the investigation of organic reaction mechanisms and molecular photochemistry. It is also very useful to study the intermolecular thermal or photochemical cycloaditions, of conjugated systems. The object of the present investigation was to analyse if the mobile π-electron system in pyridine has appreciable interaction energy to account for the experimental interaction energy in molecular crystal.

While calculating the interaction energy between a pair of molecules situated parallelly with reference to the axes of the molecules in the ground state, we have assumed that the interacting molecules are identical closed shells, with the same pattern and situated at some distances along Z-axis. The wavefunctions of the molecules in the ground state are taken as one-centre functions, which can be solved more accurately than the multi-centre wavefunctions. The centre of coordinates of the system is taken the mid-point between the two centres of the molecules. Since the molecules are spherically symmetrical both \( \rho \) and \( \Phi \) coordinates remain unchanged, only change that occurs is in the \( Z \)-coordinate. Under these assumptions the major interactions are expected to arise from the less tightly bound manifold of \( \pi \)-orbitals (and \( \pi \)-electrons) on the two molecules, the \( \sigma \)-bonds acting only as a hard core which forbids too close an approach.

The HMOs of the separate systems are expanded in the usual LCAO form (atomic orbitals \( \phi_r, \phi_p \)). This expansion leads to expressions involving atomic matrix elements of the overlap and interaction energy between 2\( p \) orbitals on the two systems (Eqs. 1 and 2).

\[
S_{rr} = \int \phi_r \phi_r \, d\tau 
\]

\[
\eta_{rr} = \int \phi_r \frac{1}{2} (v + v') \phi_r \, d\tau 
\]

The matrix element \( \eta_{rr} \) is negative and is likely to be roughly proportional to the overlap integral \( S_{rr} \). For certain quantitative calculations it will be convenient to write the proportionality explicitly as

\[
\eta_{rr}/\beta = k S_{rr} 
\]

where \( \beta \) is the resonance integral in the isolated molecule and \( k \) is a dimensionless constant.

In the present case we have taken the ground state wavefunction \( \Psi \) for the two identical molecules of pyridine \( \Psi_1 \) and \( \Psi_2 \), where,

\[
\Psi_1 = 2N \sqrt{K \rho} Z_{1} e^{-K Z_{1} \rho} e^{-\rho^2/2} \left\{ \frac{e^{\rho^2}}{2V_0 \pi^2 m R^2 \rho} \right\} \left( \frac{e^{\rho^2} + e^{\rho^2}}{\rho_1 - \rho_{1+1}} \right) \left( \frac{e^{\rho^2} + e^{\rho^2}}{\rho_1 - \rho_{1-1}} \right) 
\]

\[
\Psi_2 = 2N \sqrt{K \rho} Z_{2} e^{-K Z_{2} \rho} e^{-\rho^2/2} \left\{ \frac{e^{\rho^2}}{2V_0 \pi^2 m R^2 \rho} \right\} \left( \frac{e^{\rho^2} + e^{\rho^2}}{\rho_1 - \rho_{1+1}} \right) \left( \frac{e^{\rho^2} + e^{\rho^2}}{\rho_1 - \rho_{1-1}} \right) 
\]

where \( Z_1 = Z + R/2 \) and \( Z_2 = Z - R/2 \) and \( R \) is the total distance between the centres of the two molecules.

The overlap integral \( \langle S_{12} \rangle \) for the molecules is then given by Eq. (6).

\[
S_{12} = \int \Psi_1^{*} \Psi_2 \, d\tau 
\]

and the total interaction energy \( E \) is given by Eq. (7)

\[
E = 4 \beta_{12} S_{12} \]

where \( \beta_{12} \) is the resonance integral for the isolated molecules and is given by Eq. (8).

\[
\beta_{12} = 2.85 \beta \times S_{12} 
\]

In Eq. (8) \( \beta \) is the spectroscopic value of resonance integral of pyridine molecule which is taken as \(-3\) eV (as estimated by Hückel). The interaction energies are...
Table 1—Overlap-integral and Interaction Energies between Two Molecules of Pyridine in Ground State

<table>
<thead>
<tr>
<th>Distance (R) (Å)</th>
<th>Overlap-integral (S_{12})</th>
<th>Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.0</td>
<td>0.120</td>
<td>11.3526</td>
</tr>
<tr>
<td>1.5</td>
<td>0.443</td>
<td>154.7181</td>
</tr>
<tr>
<td>2.0</td>
<td>0.338</td>
<td>90.0665</td>
</tr>
<tr>
<td>2.5</td>
<td>0.147</td>
<td>17.0354</td>
</tr>
<tr>
<td>3.0</td>
<td>0.041</td>
<td>1.3253</td>
</tr>
<tr>
<td>3.5</td>
<td>0.008</td>
<td>0.0505</td>
</tr>
<tr>
<td>4.0</td>
<td>0.001</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

At R > 4Å, overlap-integral becomes zero.

then calculated from Eq. (7) which are negative and are given in Table 1.

We may conclude that the overlap integrals S_{12} are in good agreement with the assumption made by Lionel Salem\(^2\) that the significant range of distances (i.e. 2.5-3.5Å) where the core repulsive wall is small, the overlap is smaller than 0.2 and the magnitude of increase in overlap value is less and less until it reaches a maximum at 1.74Å and as the distance decreases even further the overlap becomes more and more negative.

The calculated energies are also in good agreement with the assumption that energy decreases as the distance increases.

In the absence of any experimental results, it is difficult to talk about the accuracy of the calculated values presented in this note.

References