CALCULATION OF THE ENERGY LEVELS OF SOME AMINONITROOLEFINS BY POPLE'S METHOD

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The semiempirical method of Pople was applied to the calculation of the energy levels and absorption bands of the \( \pi \) and \( n \) electrons in chains of the type \( \text{O}_2\text{N}(-\text{CH}==\text{CH})_n\text{NH}_2 \) for various values of \( n \). The possibility for the emergence of a cyclic structure with participation of a hydrogen bond between the nitro and the amino group was studied for \( n = 1 \). The calculation of the H bond was carried out in a two-configurational approximation involving the \( p_6 \) orbital of the hydrogen atom.

INTRODUCTION

Unsaturated nitro compounds represent an extremely interesting class of organic compounds. A variety of methods for their synthesis has been developed recently. Because of their high chemical activity, these compounds are the starting materials for the synthesis of many organic compounds. Among the numerous studies of these molecules, one must point out the work by Shvarts [1], who calculated by the MO LCAO method in the Hückel modification the energy levels, the charges at the atoms, and the bond orders in the compounds \( \text{X}--\text{CH}--\text{CH}--\text{CH}--\text{CH}--\text{Y} \), where \( \text{X} = \text{O}, \text{Nit} \) and \( \text{Y} = \text{CH}_2, \text{O}, \text{NH} \). The calculated frequencies of the absorption bands in the UV region of the spectrum are in rather good agreement with experimental data. We chose as objects of our study compounds of the type \( \text{O}_2\text{N}(-\text{CH}==\text{CH})_n\text{NH}_2 \), in which \( n \) has a value of 1, 2, 3, or 4. It is possible that the compounds with large \( n \) are unstable, but such a calculation allows one to arrive at important regularities, which coincide not only with those of their (stable) derivatives, but also with those of several other classes of similar compounds.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{Sn} \pi^* ) (eV) within NO ( \text{N} )</th>
<th>( \text{Sn} \pi^* ) (eV) from NH ( \text{N} ) to NO ( \text{N} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n=1 )</td>
<td>4.52</td>
<td>5.29</td>
</tr>
<tr>
<td>( n=2 )</td>
<td>4.26</td>
<td>4.53</td>
</tr>
<tr>
<td>( n=3 )</td>
<td>3.85</td>
<td>4.09</td>
</tr>
<tr>
<td>( n=4 )</td>
<td>3.62</td>
<td>3.47</td>
</tr>
</tbody>
</table>

1. CALCULATION FOR THE AMINONITROOLEFINS

\( \text{O}_2\text{N}(-\text{CH}==\text{CH})_n\text{NH}_2 \), with \( n = 1, 2, 3, 4 \).

We chose the semiempirical SCF MO LCAO method modified by Pople [2] for the calculation of the energy levels of the compounds under consideration. This method has been repeatedly and successfully used for the calculation of the \( \pi \)-electron density and the energies of long-wavelength transitions in organic molecules. A large part of the calculations was run on the M-20 computer.

The secular equation in the matrix form was written as

\[
\mathbf{F} \mathbf{C} = \mathbf{E} \mathbf{C},
\]

where \( \mathbf{F} \) is the matrix operator of the energy, \( \mathbf{C} \) is the matrix of coefficients \( C_{ij} \) of the molecular orbital matrix splitting, and \( \mathbf{E} \) are the energy levels. The diagonal member of matrix \( \mathbf{F} \) is

\[
F_{ii} = F_{ii}^0 + (P_{ii} - Z_i^2) \lambda_{ii} + \sum_{\alpha} 2P_{i\alpha}N_{i\alpha} - \sum_{\beta} Q_{i\beta},
\]

The nondiagonal member has the form

\[
F_{ij} = F_{ij}^0 - P_{ij} \lambda_{ij} (i = j \pm 1); \quad F_{ij} = -P_{ij} \lambda_{ij} (i \neq j \pm 1);
\]

where \( F_{ij}^0 \) are the splitting coefficients of the molecular orbitals in terms of atomic functions, \( \alpha \) is the orbital number, \( Z_i^2 \) is the charge of the corresponding nucleus, \( \gamma_{ii} \) is a one-center Coulomb integral, \( \gamma_{ij} \) is the two-center Coulomb integral of the repulsion between the electrons of atoms \( i \) and \( j \), \( Q_{ii} \) is the two-center Coulomb attraction integral between the electrons of atom \( i \) and the nucleus of atom \( j \), and

\[
F_{ij} = -\frac{1}{2} S_{ii} (I_i + I_j), \quad F_{ii} = -A_i,
\]

where \( I_i \) and \( I_j \) are the ionization potentials of atoms \( i \) and \( j \) and \( S_{ij} \) is the corresponding overlap integral.

The integrals \( \gamma_{ii} \) were taken from the tables by Preuss and the integrals \( S_{ij} \) were taken from Mulliken's tables. After determination of the energies of the one-electron levels, we calculated the energies of electronic singlet–singlet transitions without consideration of a configurational interaction according to

\[
\Delta e = \Delta e_{\text{one-electron}} - K_{ij} + 2A_{ij},
\]

where \( K_{ij} \) is a Coulomb integral and \( A_{ij} \) is a volume integral. In addition to the energies of the \( \text{Sn} \pi^* \) transitions, we calculated the energies of the \( \text{Sn} \pi^* \) transitions from an atomic \( n \) orbital to an antibonding \( \pi^* \) orbital according to a method developed by Plotnikov [3]. He had shown that the energy levels \( F_{nn} \) of the \( n \) electrons in the self-consistent field method, under the condition that an atom with \( n \) electrons possesses one \( 2p_z \) electron, are determined by the expression

\[
F_{nn} = -2I + A - \delta + 2P_{n\pi n} - P_{n\pi n} + \sum_{\alpha} 2P_{n\alpha}N_{n\alpha} - \sum_{\beta} Q_{n\beta},
\]

where \( I \) is the ionization potential, \( A \) is the electron affinity, \( \gamma_{n\pi} \) is the one-center Coulomb integral, \( k_{n\pi} \) is the volume integral of the \( n \) and \( \pi \) electrons, and \( \delta \) is...
is a value determined by $\delta = \gamma_{HF} - \gamma_{HF}$ and is equal to 0.860537 $\xi$, where $\xi$ is the Slater charge. Table 1 shows the basic results of the calculation for the compounds studied by us.

The fact comes to mind that two bands lie in the near region: the $S^{\pi}\rightarrow I$ band (symmetry $B_{1}$) and the $S^{\pi}\rightarrow II$ band (symmetry $A_{1}$). Band I corresponds almost precisely to a transition within the NO$_2$ group, while band II is connected with a charge transfer between the NH$_2$ and the NO$_2$ groups on excitation. The corresponding coefficients of the molecular orbital splitting for one of the molecules are given in Table 2. As the conjugated chain becomes longer, the bands are shifted more and more to the long-wavelength side, although the band related to the charge transfer is shifted much more rapidly and the bands intersect approximately with the fourth unit. For the longer molecules, the charge transfer band is farthest in the red region. It should be pointed out that the relative position of the bands with and without charge transfer depends to a significant degree on the effects of electron correlations, which are not considered in our discussion. Consequently, the results presented here must be regarded as preliminary results which are to be refined by inclusion of configurational interactions. The band of the $S^{\pi}\rightarrow$ transition from an atomic orbital to an antibonding $\pi^*$ orbital is also shifted toward the red side as the conjugation chain is increased. In a short molecule, its frequency is lower than the frequencies of the $S^{\pi\pi}$ transitions. The intersection of the $S^{\pi\pi}$ transition with the $S^{\pi\pi}$ transition occurs approximately with the fourth unit. Similar results on intersections of $S^{\pi\pi}$ and $S^{\pi\pi}$ transition bands were first obtained in [3] and [4].

As is seen from the molecular diagrams (Fig. 1), as the chain becomes longer, the single and double bonds tend to level out; in other respects, the distribution of the electron density in these compounds differs little from one compound to another.

**Table 2**  
One-Electron Levels and Splitting Coefficients of Molecular Orbitals of the Molecule

<table>
<thead>
<tr>
<th>$E$</th>
<th>$C_0$</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
<th>$C_5$</th>
<th>$C_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.3</td>
<td>0.179</td>
<td>-0.179</td>
<td>-0.345</td>
<td>0.654</td>
<td>-0.595</td>
<td>0.140</td>
<td></td>
</tr>
<tr>
<td>20.4</td>
<td>0.470</td>
<td>-0.520</td>
<td>-0.024</td>
<td>0.484</td>
<td>-0.023</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.96</td>
<td>0.289</td>
<td>-0.389</td>
<td>-0.771</td>
<td>0.284</td>
<td>0.123</td>
<td>0.078</td>
<td></td>
</tr>
<tr>
<td>1.772</td>
<td>-0.107</td>
<td>-0.107</td>
<td>-0.122</td>
<td>0.186</td>
<td>0.470</td>
<td>0.836</td>
<td></td>
</tr>
<tr>
<td>0.530</td>
<td>0.075</td>
<td>-0.756</td>
<td>0.005</td>
<td>0.001</td>
<td>0.013</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>0.4456</td>
<td>-0.290</td>
<td>-0.280</td>
<td>0.024</td>
<td>0.675</td>
<td>0.468</td>
<td>-0.456</td>
<td></td>
</tr>
</tbody>
</table>

All values are given in $3$ units; $3 = -4.79$ eV.

2. **CALCULATION OF THE H-BONDS**

Spectral studies [5] of substituted O$_2$N(--CH=CH--)$_n$NH$_2$ compounds have shown that an absorption maximum occurs in the 225-250 $\mu$m region. The authors [6] did not detect bands characteristic for the nitro group in the spectra of these compounds.

![Molecular diagrams of aminonitroolefins](image)

A detailed study of the infrared spectra of these compounds [5] has shown that the vibrational frequency of the amino group and the double bond is significantly reduced. These facts lead to the assumption that the existence of a hydrogen bridge and a cyclic structure of the compound with $n = 1$ exists and that an enamine form is possible.

We calculated the stabilization energy for the transition from the form O$_2$N--C=C--NH$_2$ to the form

![Molecular diagram](image)

The calculation was first performed in the Pople approximation with several improvements, namely consideration of the contribution made by the first excited configuration to the ground state. The necessity of such an improvement had been shown first by Pullman and Pullman [7]. The wave function was written in the form

$$\Psi_{total} = C_0 \Psi_0 + C_1 \Psi_1$$

and the coefficients $C_0$ and $C_1$ were determined by the variation method. At first, the stabilization energy was calculated on formation of a ring without consideration of a hydrogen bond. The results showed that the energy gain in going from the chain to the ring configuration is equal to $-10$ kcal/mole. The frequency of the longest wavelength transition is equal to 4.43 eV. The N-H...O bond was taken into consideration in the subsequent stage of the study. To explain the properties of the hydrogen bond Shigorin [8] proposed including the participation of $\pi$ electrons in its formation. The total energy of the hydrogen bond