On the possibility of excimer state formation in homodimers of the pyrimidine bases.

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ABSTRACT

A detailed investigation of the ground state and the first excited state of the pyrimidine bases of uracil, cytosine, thymine and their stacked homodimers is carried out by the Extended Hückel method. The first excited state is shown to be the $\pi^*$-state. The excitation is localized mainly on the C-C bond region.

The energy dependence of the ground state and the first excited state of the homodimers on the mutual position of bases is considered. For every dimer a minimum on the excited state potential curve is found. This fact creates the possibility for the formation of excimer. The obtained data give some reason for the suggestion about participation of the excimer state as a precursor of photodimer.

INTRODUCTION

The lethal and mutagenic action of ultraviolet light is mainly caused by formation of photodimers of the pyrimidine bases as was shown in a series of papers [1-3]. The important biological consequences of photodimerization caused the appearance of a number both experimental [4,5] and theoretical [6-11] data on the study of mechanism of this UV-induced reaction.

In the works devoted to the investigation of kinetics of photodimerization quenching [12] a scheme was proposed according to which photodimerization of the pyrimidine bases does not proceed directly from the excited states as was suggested before but includes an intermediate stage—formation of an excimer as a precursor of photodimer.

Evidence for the possibility of forming the excimer sta-
te may be given by a minimum on the potential energy curve of the bases interaction versus interplanar separation. At present the only practically available method which gives the possibility to calculate the potential energy curves for complex molecules in the ground and the excited states is the Extended Hückel (EH) Treatment. Unfortunately this is a restricted method. It takes into account intermolecular interactions in the complexes effectively only and does not distinguish between the triplet and the singlet excited states. However it was successfully used in [13-15] for calculating different characteristics of the excimer state of ethylene and a series of aromatic hydrocarbons: benzene, naphthalene and some of their derivatives.

MODEL AND METHOD OF CALCULATION

To elucidate the possibility of participation of the excimer state as a precursor of photodimer we have investigated the energy dependence of the ground state and the first excited state of the pyrimidine homodimers on the mutual position of bases by the EHT. Calculations were done using the Hoffmann parameters [16]. The resonance integrals were approximated both by the Wolfsberg-Helmholtz [17] and the Cusachs's [18]expressions. The geometry for each of the pyrimidine bases was taken from the data of Spencer [19], the methyl group geometry of thymine was chosen to be the same as in paper [20].

As calculation of the systems being an object of our investigation is a rather labourous task the complexes of the pyrimidine bases were calculated in regular sandwich configuration the most favourable for formation of an excimer. Furthermore, some irregular sandwich configurations were also studied. These were formed as a result of translation of one monomer relatively to another one and/or by the rotation around the axis perpendicular to the monomer plane and by the simultaneous translations and rotations. The calculation of the distance-dependent potential curves for the homodimers was carried out by changing the vertical distance between the monomer planes.
To obtain the most stable configuration of the thymine dimer the dependence of the interaction energy on relative position of the methyl group was investigated. In so doing the cis-syn, cis-anti, trans-syn, trans-anti thymine dimer configurations were studied for the minimization H-atoms repulsion of the methyl groups.

RESULTS AND DISCUSSION

The distance-dependent interaction potential curves for the pyrimidine homodimers of uracil, cytosine and thymine in the ground and the first excited states are indicated in Fig.1. One may see that for all potential curves of the excited state of the pyrimidine homodimers (which is the $H, H^*$ state) a minimum is observed; that is there exists the possibility of formation of the excimer state.

![Fig.1. Distance-dependent interaction potential curves for the pyrimidine homodimers in the ground and first excited states.](image)
The calculated stabilization energy of the excimer state ($\Delta E_{ex}$) and the equilibrium intermolecular distance ($\Delta Z_0$) for UU, CC and TT dimers are given in Table 1 for the Wolfsberg-Helmholts and the Cusachs's approximations. One should note that equilibrium distances for every dimer are the same for different approximations of resonance integrals whereas the stabilization energies are different. It was shown the regular sandwich configuration (cis-syn) of homodimers had the maximal stabilization energies.

Table 1. Excimer state characteristics of homodimers of the pyrimidine bases

<table>
<thead>
<tr>
<th>Homodimer</th>
<th>Wolfsberg-Helmholts approximation</th>
<th>Cusachs approximation</th>
<th>Wolfsberg-Helmholts approximation</th>
<th>Cusachs approximation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta Z_0$ (Å)</td>
<td>$\Delta E_{ex}$ (kcal/mole)</td>
<td>$\Delta Z_0$ (Å)</td>
<td>$\Delta E_{ex}$ (kcal/mole)</td>
</tr>
<tr>
<td>UU</td>
<td>3.0</td>
<td>7.1</td>
<td>3.1</td>
<td>8.8</td>
</tr>
<tr>
<td>CC</td>
<td>3.2</td>
<td>5.5</td>
<td>3.2</td>
<td>6.9</td>
</tr>
<tr>
<td>TT</td>
<td>3.8</td>
<td>1.8</td>
<td>3.8</td>
<td>3.7</td>
</tr>
</tbody>
</table>

In connection with the finding of a minimum on the potential energy curve of the excited state it was very interesting to investigate the change in the electronic distribution at the transition of monomers and dimers from the ground state to the excited state. The analysis of calculated the atomic charges and orbital overlap populations showed [27] the excitation is localized on the C2-C6 bond of both monomers and dimers. In this connection it should be noticed that the same conclusion [6] was found by simple Hückel method for the investigation of isolated bases.

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