Halogen-Substitution Effect on the Optical Absorption Bands of Uracil

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The ultraviolet absorption spectra of uracil and its 5-halogenated derivatives have been investigated in regard to the electron attracting properties of the substituents. It could be shown that the position of the two absorption bands is proportional to the inverse of the electronegativity; the extinction coefficients are a linear function of the electron affinities. In this way, the red shift obtained upon substitution with halogens can be explained.

Also, the decrease in absorbance of the absorption bands at \( \lambda > 250 \text{ nm} \), occurring concomitantly, is understandable. The increase in absorbance with increasing electron affinity, as observed in the case of the absorption bands at \( \lambda < 250 \text{ nm} \), might question the assumption that this band is due to a higher \( \pi - \pi^* \) excitation.

Introduction

Because of their widespread application in and of their importance for biological systems the chemical and physicochemical properties of halogenated uracil derivatives have been investigated to some detail. The optical absorption spectra have been of special interest since they reveal, for example, some information about radiation damage and dissociation constants. It could be shown that a halogen substitution at the 5-position of uracil results in a red shift and change in intensity of the two absorption bands. Several mechanisms have been proposed for explaining this observation. A detailed explanation, however, could not be given yet. Investigating the pH dependence of the UV absorption spectra of the halogenated uracils, Berens and Shugar noted a dependence of the bathochromic shift on the electronegativity of the halogen substituents. However, they did not give any quantitative description; they limited their observations to the absorption band occurring at \( \lambda > 250 \text{ nm} \); for these bands they gave only a qualitative description about the dependence of the extinction coefficients on the electron affinities of the substituents. In this communication a systematic investigation was conducted in regard to the dependence of the absorption maxima as well as the extinction coefficients of both of the absorption bands upon the electron-attracting property of the substituents.

Material and Methods

The following compounds were investigated: Uracil (Ura) and its fluoro, chloro, bromo, and iodo analogues substituted at the 5-position (5 F\text{Ura}, 5 Cl\text{Ura}, 5 Br\text{Ura}, 5 I\text{Ura}). These substances were supplied by Merck AG, Darmstadt, and were used without further purification.

The compounds were dissolved in bidistilled water; their absorption spectra were recorded with a Cary 14 spectrophotometer. A constant concentration of 0.1 mM was used throughout the experiments.

Results and Discussion

The absorption spectra of Ura and its 5-halogenated derivatives are shown in Fig. 1. For simplicity, for a few of the compounds only the absorption maxima are given. The absorption bands at \( \lambda > 250 \text{ nm} \) (in the following referred to as second band) are thought to be due to a \( \pi - \pi^* \) excitation of the C5 — C6 double bond, while the absorption bands at shorter wavelength (in the following referred to as first band) are supposed to be associated with a higher \( \pi - \pi^* \) excitation. Halogen substitution at the 5-position causes a red shift of both of the absorption bands it is, however, more expressed at the second band. The intensity (absorbance) of the second band decreases while it behaves inversely for the band at \( \lambda < 250 \text{ nm} \). The absolute change in intensity is more pronounced in the case of the first band.

* Dedicated to Professor Dr. H.-J. Born on the occasion of his 65th birthday.
The position of the two absorption bands of the compounds investigated and their intensities (in arbitrary units) are summarized in Table I. Moreover, the electron affinities (EA) and the electronegativities (EN, according to the Pauling scale) are given.

Table I. Characteristic properties of uracil and its halogenated derivatives used in text (wavelengths and intensities were taken from Fig. 1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>EN (kcal/g ion)</th>
<th>EA (kcal/g ion)</th>
<th>1st. Band λ (nm)</th>
<th>Intensity (arb. units)</th>
<th>2nd. Band λ (nm)</th>
<th>Intensity (arb. units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>uracil</td>
<td>2.20</td>
<td></td>
<td>202.4</td>
<td>22.7</td>
<td>258.4</td>
<td>20.6</td>
</tr>
<tr>
<td>F-</td>
<td>3.98</td>
<td>79.5</td>
<td>203.3</td>
<td>22.3</td>
<td>265.3</td>
<td>18.8</td>
</tr>
<tr>
<td>Cl-</td>
<td>3.16</td>
<td>83.2</td>
<td>210.9</td>
<td>22.3</td>
<td>274.1</td>
<td>18.5</td>
</tr>
<tr>
<td>Br-</td>
<td>2.96</td>
<td>77.5</td>
<td>211.3</td>
<td>25.3</td>
<td>277.3</td>
<td>18.7</td>
</tr>
<tr>
<td>I-</td>
<td>2.66</td>
<td>70.5</td>
<td>216.5</td>
<td>30.1</td>
<td>283.5</td>
<td>15.8</td>
</tr>
</tbody>
</table>

A plot of the wavelength of the absorption maxima of the two absorption bands (λ opt. of first and second band, resp.) vs the inverse of the electronegativity results in a fairly good linear relationship (s. Fig. 2). It is interesting to note that there seems to be a difference in the dependency of the wavelengths of the two absorption bands on EN. The same effect was observed with the intensities. In this case, however, the change of the first band is more pronounced, and the changes of the two bands are opposite.

The dependence of the intensity (in arbitrary units) on the electron affinities of the halogens is shown in Fig. 3. Again, a linear relationship seems to exist.

From the results obtained one might conclude that the position and the extinction coefficients of the absorption bands of uracil and its derivatives depend upon the electronegativity and the electron affinity, resp., of the substituents in the 5-position. In this way, the results seem to favor the mesomeric effect according to which the space available for the π-electrons is enlarged by the substituents. This results in a red shift and in a decrease of the intensities. The increase in intensity of the first absorption band, however, cannot be explained yet although this parameter, too, seems to depend on the electron affinity of the substituent.
The excellent technical assistance of Miss A. Dimmerling and Mrs. U. Behrens is greatly appreciated.

1 W. Bruder and W. Lohmann, Studia Biophysica, Berlin 34, 189 [1972].
3 W. Szybalski, Radiation Res. Suppl. 7, 147 [1967].

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