Halogen-Substitution Effect on the Optical Absorption Bands of Uracil*

Wolfgang Lohmann

Institut für Biophysik der Universität, Giessen, and Abteilung für Biophysikalische Chemie, GSF, Neuherberg

(Z. Naturforsch. **29 c**, 493–495 [1974]; received March 18/April 26, 1974)

Halogen Effect, Absorption Bands, Uracil, Electron Affinity, Electronegativity

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 $\lambda > 250$ nm, occuring concomitantly, is understandable. The increase in absorbance with increasing electron affinity, as observed in the case of the absorption bands at $\lambda < 250$ 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 ingestigated to some detail. The optical absorption spectra have been of special interest since they reveal, for example, some information about radiation damage [1–3] and dissociation constants [4]. 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 [4, 5]. Several mechanisms have been proposed for explaining this observation [4, 6]. 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 [4] 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 occuring at $\lambda > 250$ 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.

Requests for reprints should be sent to Prof. Dr. W. Lohmann, Institut für Biophysik der Universität, Leihgesterner Weg 217, *D-6300 Giessen*, Germany.

Material and Methods

The following compounds were investigated: Uracil (Ura) and its fluoro, chloro, bromo, and iodo analogues substituted at the 5-position (5 FUra, 5 ClUra, 5 BrUra, 5 IUra). 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 $\lambda > 250$ nm (in the following referred to as second band) are thought to be due to a pi – pi* excitation of the $C_5 - C_6$ double bond [6], 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 $\lambda < 250$ 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.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung") beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

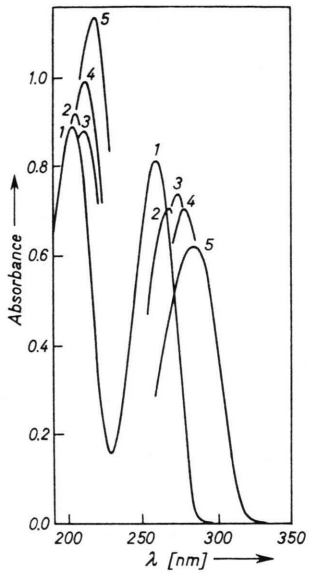

Fig. 1. Absorption spectra of uracil and its 5-halogenated derivatives (solvent: H_2O). 1. 0.1 mM uracil; 2. 0.1 mM F-uracil; 3. 0.1 mM Cl-uracil; 4. 0.1 mM Br-uracil; 5. 0.1 mM I-uracil.

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 [7] (EA) and the electronegativities [8] (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).

Compound		EN	EA [kcal/g ion]	1st. Band λ [nm]	1st. Band Intensity [arb. units]	2nd. Band λ [nm]	2nd. Band Intensity [arb. units]
	uracil	2.20		202.4	22.7	258.4	20.6
F-	"	3.98	79.5	203.3	23.3	265.3	17.8
Cl-	"	3.16	83.2	210.9	22.3	274.1	18.5
Br-	"	2.96	77.5	211.3	25.3	277.3	17.8
I-	"	2.66	70.5	216.5	30.1	283.5	15.8

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

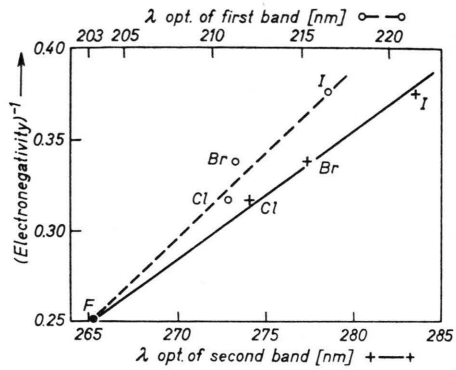

Fig. 2. The inverse of the electronegativity *vs* the wavelengths of the two absorption bands of each sample (values were taken from Fig. 1).

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.

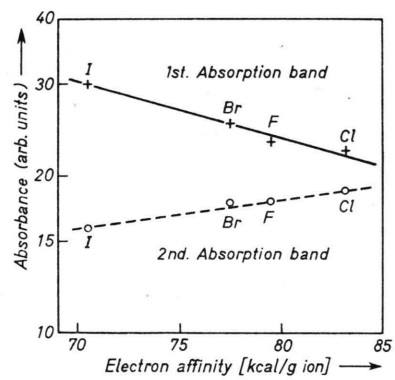

Fig. 3. The intensities (absorbance) of the two absorption bands of each sample *vs* the electron affinities of the halogens (values were taken from Fig. 1).

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. This work was supported in part by the Fraunhofer-Gesellschaft.

[1] W. Bruder and W. Lohmann, Studia Biophysica, Berlin **34,** 189 [1972].
[2] W. Lohmann, Proceedings of an International Atomic Energy Agency Panel on "Modification of Radiosensitivity in Biological Systems", Stockholm 1973, in press.
[3] W. Szybalski, Radiation Res. Suppl. **7,** 147 [1967].
[4] K. Berens and D. Shugar, Acta Biochimica Polonica **10,** 25 [1963].
[5] J. N. Murrell, "Elektronenspektren organischer Moleküle", Bibliographisches Institut, Mannheim 1967.
[6] A. Thoth and F. Billes, Acta Chim. Sci. Hung. **56,** 229 [1968].
[7] Values from Handbook of chemistry and physics, 51st. edit., p. E-73, Cleveland, Ohio: The Chemical Rubber Co. 1970–1971.
[8] Values from Electrons and chemical bonding, p. 72 (H. B. Gray, ed.), W. A. Benjamin, Inc., New York 1965.