Ultraviolet Absorption Spectra of Substituted Phenylureas. Part II[1]. *Solvent Effect and Structure of Carbamide Group*

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(Received April 11, 1960)

In the previous paper dealing with the ultraviolet absorption spectra of substituted phenylureas it was suggested that the carbamide group $-NHCONH_2$ behaves electronically as a peculiar substituent[1].

With disubstituted benzenes in general Doub and Vandenbelt found some semiquantitative relationships[2], which exist between the absorption displacement $\Delta\lambda$ and the electronic properties of the two substituents. Applying these empirical rules to the previous results, it has now been confirmed that the substituent $-NHCONH_2$ behaves as an electron-attracting or releasing group according as the other substituent is electron-releasing or attracting. During the course of an investigation of the unusual property of this group, attention has been drawn to the data given by Schroeder[3] of the spectra of ethyl phenylureas.

As is shown in Table I, *N*-ethyl phenylureas show markedly decreased intensity of absorption, whereas *N'*-ethyl derivatives exhibit strong

TABLE I. ULTRAVIOLET ABSORPTION SPECTRA OF ETHYL PHENYLUREAS (IN ETHANOL)

	$\lambda_{1\,max}$	$\varepsilon_{1\,max}$	$\lambda_{2\,max}$	$\varepsilon_{2\,max}$
$C_6H_5NHCON'H_2$	237	17,700	268～275	1,100
$C_6H_5NC_2H_5CON'H_2$	235～237	3,480	no absorption	
$C_6H_5NC_2H_5CON'HC_2H_5$	243	3,630	no absorption	
$C_6H_5NHCON'HC_2H_5$	240～241	19,800	275～277	1,000
$C_6H_5NHCON'(C_2H_5)_2$	239～241	18,300	270～273	1,100

TABLE II. ABSORPTION SPECTRA OF PARA-SUBSTITUTED PHENYLUREAS IN AQUEOUS, ALCOHOLIC AND ETHEREAL SOLUTION

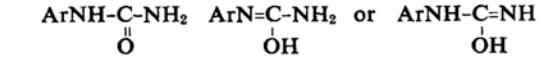
Compounds	Absorption bands	Solvent		
		Water	Ethanol	Ether
$C_6H_5NHCONH_2$	λ_1	234	287	237.5
	ε_1	6,420	18,800	19,000
	λ_2	no absorption	274	275
	ε_2	〃	1,200	1,160
p-$C_2H_5OC_6H_4NHCONH_2$	λ_1	236.5	242	243.5
	ε_1	12,800	18,200	19,300
	λ_2	280	290	293.5
	ε_2	1,860	1,980	2,180
p-$CH_3C_6H_4NHCONH_2$	λ_1	236	240	241.5
	ε_1	12,400	18,400	20,100
	λ_2	272～276	281	281
	ε_2	650	1,090	1,290
p-$NO_2C_6H_4NHCONH_2$	λ_1	325～329	322	321.5
	ε_1	10,700	13,200	14,500
	λ_2	no absorpt.	no absorpt.	no absorpt.
	ε_2	〃	〃	〃
p-$CH_3OC_6H_4NHCONH_2$	λ_1	235	237	242
	ε_1	12,900	17,700	18,200
	λ_2	279	284.5	293.5
	ε_2	1,990	1,870	2,700

1) Part I. Y. Tsuzuki, S. Motoki and K. Migita, This Bulletin, 32, 1189 (1959).

2) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, 69, 2714 (1947).

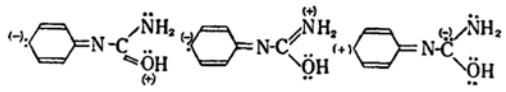
3) W. A. Schroeder, *Anal. Chem.*, 23, 1740 (1951).

absorption, as is observable in phenylurea itself. Since this effect of the alkyl group is likely to be observed in general when prototropy is set up in the systems[4], the following tautomerism (I, II, and III form) may be possible, and hence aryl ureas may, at least partly, be present in the pseudo form II. This form is impossible for *N*-alkyl phenylureas, which exhibit less intense absorptions.



(I) (II) (III)

The electronically amphoteric property of the carbamide group is thus clearly shown with the following resonance structures of the isomer.



(IV) (V) (VI)

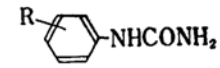
The presence of an acidic, enolizable hydrogen atom in the carbamide group is also supported by the fact that phenylureas are more soluble in aqueous alkalis than in water. From these considerations it becomes a theme of some interest to study the solvent effect on the spectra of these compounds for the purpose of getting further information on the nature of the group. In the present study were used some solvents of different polarity, such as water, ethanol and ethyl ether.

Results and Discussions

The experimental results are given in Tables II and III. It is clearly seen that the absorption intensity of the compounds increases markedly, as the polarity of the solvent decreases.

Now the remarkable solvent effect seen in Tables II and III should be considered. With common substances the extinction coefficient is, however, only slightly (5~7%) affected by the solvent, whereas the above cases are entirely different, namely ε_1 and ε_2 radically change on the whole according to the solvent. These remarkable solvent effects are occasionally observed by dissolving substances in such solvents as bring about some very mild chemical changes, as complex formation or displacement of tautomeric equilibrium[5]. Thus the data of the absorption spectrum are reasonably interpreted by assuming that in less polar solvents the equilibrium of tautomerism of aryl ureas moves towards the acidic pseudo form II which absorbs more intensely than the normal form I.

Table III. Absorption spectra in solution of ethoxyl and methoxyl phenylureas



Absorption	Solvent: Water	Ethanol	Ether
(a) R=*p*-C_2H_5O			
λ_1	236.5	242	243.5
ε_1	12,800	18,200	19,300
λ_2	279	290	293.5
ε_2	1,860	1,980	2,180
(b) R=*m*-C_2H_5O			
λ_1	238	240.5	242
ε_1	10,400	13,500	14,800
λ_2	278	280	280
ε_2	2,360	2,550	3,000
(c) R=*o*-C_2H_5O			
λ_1	236	241	242
ε_1	8,820	15,400	16,300
λ_2	278	281	281
ε_2	2,860	3,830	3,600
(d) R=*p*-CH_3O			
λ_1	235	237	242
ε_1	12,900	17,700	18,200
λ_2	279	284.5	293.5
ε_2	1,990	1,870	2,700
(e) R=*m*-CH_3O			
λ_1	238	236	241.5
ε_1	11,600	13,700	16,500
λ_2	277.5	275	280
ε_2	3,280	2,570	2,800
(f) R=*o*-CH_3O			
λ_1	237	236	241.5
ε_1	8,810	15,500	16,500
λ_2	277.5	275.5	281
ε_2	3,210	4,050	3,900

Another outstanding feature noticeable in Tables II and III is the blue shift of the absorption bands which shift further as the polarity of the solvent increases, however, with a few exceptions of *p*-nitro-, *m*-methoxy- and *o*-methoxy-phenylureas. This feature is peculiar, for increasing polarity of the solvent usually causes on the contrary a red shift of the absorption band[6].

To see clearly the effect of orientation (*o*, *m* and *p*-RO) on the red shift in ethoxy- and methoxy-phenylureas, the data in Table III were analyzed and the results are shown in Table IV.

4) See A. E. Gillam and E. S. Stern, " Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", 2nd Ed., Edward Arnold Publishers, London (1957), p. 259.

5) A. E. Gillam and E. S. Stern, loc. cit., pp. 301—2. Cf. L. N. Ferguson, *Chem. Revs.*, 43, 394 (1948).

6) A. E. Gillam and E. S. Stern, loc. cit., p. 303.

TABLE IV. ORIENTATION EFFECT ON BATHOCHROMIC SHIFT IN ETHOXYL AND METHOXYL PHENYLUREAS (ANALYSIS OF THE ABSORPTION DATA IN TABLE III)

Solvent	Compound	Relation	
		K-band	B-band
Ether	$C_2H_5OC_6H_4NHCONH_2$	$p>o=m$	$p\gg o>m$
Ether	$CH_3OC_6H_4NHCONH_2$	$p>o=m$	$p\gg o>m$
Ethanol	$C_2H_5OC_6H_4NHCONH_2$	$p>o>m$	$p\gg o>m$
Ethanol	$CH_3OC_6H_4NHCONH_2$	$p>o=m$	$p\gg o>m$
Water	$C_2H_5OC_6H_4NHCONH_2$	$m>p>o$	$p>o=m$
Water	$CH_3OC_6H_4NHCONH_2$	$m>o>p$	$p>o=m$

From Tables III and IV is noticed a third interesting phenomenon, namely, for B-band the absorption maximum of the alkoxy-phenylureas is in the order $p\gg o>m$ in both ethanol and ether, while in aqueous solution the three nuclear isomers absorb nearly the same wave length region; for the K-band, *m*-compounds absorb in aqueous solution the region of the longest wavelength ($m>p=o$), although the former relation $p>o>m$ nearly holds in ethanolic and ethereal solution.

These somewhat peculiar relations may be interpreted, at least partly, by the idea that in aqueous solution the carbamide group mainly takes the urea form, so that it loses the electron-attracting property as the result of the absence of resonance with the alkoxyl group, but in non-aqueous solutions the carbamide group assumes a greater part of the pseudo form, making the resonance possible with the alkoxyl group.

Thus the pseudo form of phenylureas is assumed and may be confirmed from various angles. For this purpose it is desirable to synthesize some of the pseudo derivatives, and to make a special study of the spectrum[7]. The result of this study will be reported in the next paper.

Experimental

Preparation of Compounds.—Substituted phenylureas were prepared from potassium cyanate and the corresponding nuclear substituted anilines by the methods described in "Organic Syntheses"[8]. *o*-Methoxyl phenylurea, m. p. 146.5°C, *m*-isomer, m. p. 130°C, *p*-isomer, m. p. 164~5°C. The solvents were purified by distillation. Ethanol was tested to be free from benzene.

Absorption Spectra.—The absorption spectra were measured in the region of 200~350 mμ by means of a Beckmann Model DU Quartz spectrophotometer with the solutions of concentration about 1/10,000 M.

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7) See A. E. Gillam and E. S. Stern, loc. cit., p. 257.
8) F. Kurzer, "Organic Syntheses", Vol. 31, John Wiley & Sons, Inc. New York (1951), p. 8.