Ultraviolet Absorption Spectra of Substituted Phenylureas

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Dulcin(*p*-ethoxypenylurea) has been a well known substance as one of the strongest sweetening agents, whereas the ortho isomer is tasteless and the *m*-ethoxyphenylurea rather bitter.

In an earlier work on the sweetness of organic compounds one of the authors has pointed out that the sweetness of aromatic compounds is closely related to the resonance structures, and has shown that the greater the sweetness of the compound, the greater is the resonance energy[1]; thus, the resonance energy in dulcin isomers decreases in the order of $p>o>m$.

Since the ethoxy group, being associated with the carbamide group, would contribute to the resonance stabilization of the molecule in different ways to cause electronic effects according to the relative position of the two groups, the mode of the resonance in these compounds could be analyzed, provided the electronic nature of the carbamide group is elucidated. The purpose of this paper is to obtain whatever information is possible on these problems.

As is well known the ultraviolet absorption spectrum of benzene exhibits the characteristic peaks at 203.5 mμ (K-band, $\varepsilon=7400$) and 240~260 mμ (B-band, $\varepsilon=250$). When a substituent is introduced into the nucleus, both of the absorption bands are displaced towards the region of longer wavelengths owing to the resonance attributed to the conjugation of the substituent with the nucleus. In disubstituted benzenes the following semiquantitative relations have been established by Doub and Vandenbelt[2,3] between the absorption displacement and the electronic properties of the two groups, thus:

1. In the absorption spectrum of the disubstituted benzenes, one substituent of which is electron-attracting and the other electron-releasing.

a) The absorption shift of the 203.5 mμ band of benzene is, in the case of *p*-compounds ($\Delta\lambda$), considerably greater than the sum of those of the corresponding monosubstituted compounds ($\Delta\lambda_1+\Delta\lambda_2$), namely,

$$\Delta\lambda \gg \Delta\lambda_1+\Delta\lambda_2$$

Example:

	p-$H_2N\cdot C_6H_4\cdot NO_2$		$C_6H_5NO_2$		$C_6H_5NH_2$
λ_{max} (mμ)	381		268.5		230
$\Delta\lambda$ (mμ)	177.5	$\gg$	65	+	26.5
	$\Delta\lambda$		$\Delta\lambda_1$		$\Delta\lambda_2$

b) As to the orientation effect, the following order of red-shift is observed:

$$\lambda_{max}\ p>o>m$$

Example:

$H_2N\cdot C_6H_4\cdot NO_2$	*p*	*o*	*m*
K-band	381	282.5	280
B-band	—*	412	358

2. In the spectra of disubstituted benzenes the groups of which are both electron-attracting or both electron-releasing.

a) In the case of *p*-compounds:

$$\Delta\lambda<\Delta\lambda_1+\Delta\lambda_2$$

Example:

	p-$NO_2\cdot C_6H_4\cdot CO_2H$		$C_6H_5NO_2$		$C_6H_5\cdot CO_2H$
$\Delta\lambda$ (mμ)	55	<	65	+	26.5

b) In the case of nuclear isomers:

$$\lambda_{max}\ p>m>o$$

Example:

$H_2N\cdot C_6H_4\cdot NH_2$	*p*		*m*		*o*
K-band	245	>	240	>	233
B-band	320	>	289	$\geqq$	289

3. In the spectra of disubstituted benzenes, one substituent of which is a halogen atom or a methyl radical.

a) In the case of *p*-compounds:

$$\Delta\lambda \geqq \Delta\lambda_1+\Delta\lambda_2$$

This relation always holds, regardless of whether the electronic property of the other substituent be electron-attracting or electron-releasing.

b) In the case of three isomers:

$$\lambda_{max}\ p>m>o$$

1) Y. Tsuzuki, S. Kato and H. Okazaki, *Science [Japan] (Kagaku)*, **24**, 523 (1954).
2) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).
3) L. Doub and J. M. Vandenbelt, ibid., **71**, 2414 (1949).

* The absorption corresponding to the B-band often disappeared with *p*-compounds.

Few exceptions have been, however, found in this case.

On the basis of these empirical rules, one might determine, by means of spectroscopy, the stabilization due to resonance in disubstituted benzenes and the electronic effect of the substituent.

In the present investigation several substituted phenylureas containing various substituents of typical electronic nature such as NO_2, EtO, CH_3, Br were prepared and the spectra of these compounds were measured for the purpose of determining the electronic effect of the carbamide group and comparing with each other the magnitudes of the resonance of the nuclear isomers of dulcin.

Results and Discussion

The experimental results are shown in Table I.

TABLE I. ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED PHENYLUREAS ($R \cdot C_6H_4 \cdot NHCONH_2$)

Substituent R	K-band λ_{max}	K-band ε_{max}	B-band λ_{max}	B-band ε_{max}
o-NO_2	275	4350	365	3260
m-NO_2	270	5130	338	1660
p-NO_2	322	13200	—	—
o-EtO	241	15400	281	3830
m-EtO	240.5	13500	280	2550
p-EtO	242	18200	290	1980
o-CH_3	236	10400	270	660
m-CH_3	240	17600	277	770
p-CH_3	240	18400	281	1090
p-Br	247	25300	276	1370

Table II is given to see how the above stated relations are applicable to the present results. It is seen from this table that the absorption maxima of the three isomers $EtO \cdot C_6H_4 \cdot NHCONH_2$ appear in the order of $p>o>m$ for both K- and B-bands. The results may be interpreted as indicating the resonance energy decreasing in the order $p>o>m$, which shows that the carbamide group is electron-attracting. The conclusion is well in accordance with the tentative theory of the relation between the sweetness and the resonance. On the other hand, the slight resemblance of the spectra of nitrophenylureas to those of nitroaniline rather leads us to a somewhat opposite conclusion that the carbamide group is slightly electron-releasing.

TABLE II. ANALYSIS OF ABSORPTION DATA

a) *p*-Substituted phenylureas

p-$R \cdot C_6H_4 \cdot NHCONH_2$

Substituent R	Relation				
	$\Delta\lambda$	>	$\Delta\lambda_1$**	+	$\Delta\lambda_2$
NO_2	118.5	>	33.5	+	65
	$\Delta\lambda$	<	$\Delta\lambda_1$	+	$\Delta\lambda_2$
EtO	38.5	<	33.5	+	16
	$\Delta\lambda$	=	$\Delta\lambda_1$	+	$\Delta\lambda_2$
CH_3	36.5	=	33.5	+	3
	$\Delta\lambda$	>	$\Delta\lambda_1$	+	$\Delta\lambda_2$
Br	43.5	>	33.5	+	6.5

b) Nuclear isomers of substituted phenylureas

Substituent R	Relation	
	K-band	B-band
NO_2	$p>o>m$	$o>m$
EtO	$p>o>m$	$p>o>m$
CH_3	$p=m>o$	$p>m>o$

It follows therefore that this group is to be regarded as electronically amphoteric, behaving in an electron-attracting or releasing manner, depending on the other group.

Since such a peculiar organic group has never been known in the chemical literature, further investigation is now being made to ascertain the new interpretation of these structural problems, the results of which will be published in the near future.

Experimental

Preparation of Samples. — Commercial dulcin was used after purification by repeated recrystallization from water.

o-Nitrophenylurea was synthesized according to the direction of Arndt[4] with slight modification.

$$o\text{-}NO_2C_6H_4NH_2HCl \xrightarrow[NaOH]{Pb(SCN)_2} (o\text{-}NO_2C_6H_4NHCSNH_2)$$

$$\xrightarrow[-H_2S]{} o\text{-}NO_2C_6H_4NHCN \xrightarrow[HCl]{H_2O} o\text{-}NO_2C_6H_4NHCONH_2$$

The other substituted phenylureas were prepared from potassium cyanate and the corresponding nuclear substituted anilines by the methods given in "Organic Syntheses"[5].

o-Nitrophenylurea, m. p. 183~184°C, the *m*-isomer, m. p. 189°C, the para, m. p. 235°C.

o-Ethoxyphenylurea, m. p. 134°C, the *m*-isomer, m. p. 112°C, the para, m. p. 175°C.

o-Methylphenylurea, m. p. 195°C, the *m*-compound, m. p. 145°C, the para, m. p. 183°C.

p-Bromophenylurea m. p. 220°C.

** Phenylurea has two absorption peaks at 237 mμ (ε=17700) and 266~275 mμ (ε=1100) corresponding to K-band and B-band, respectively. W. A. Schroeder et al., *Anal. Chem.*, **23**, 1740 (1951).

4) F. Arndt, *Ber.*, **46**, 3528 (1913).

5) F. Kurzer, "Organic Syntheses", Vol. 31, John Wiley & Sons, Inc., New York (1951), p. 8.

Absorption Spectra.—The absorption spectra were measured in the region of 200~350 mμ by means of a Beckman Model DU Quartz spectrophotometer with the above samples dissolved in absolute ethanol to the concentration of ca. 1/10,000 mol./l.

Summary

Ultraviolet absorption spectra of several nuclear substituted phenylureas have been measured with the attempt to study the electronic effect of the carbamide group, and the resonance stabilization in three dulcin isomers.

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