

Effects of substituents on the electronic absorption spectra of 3-*N*-(4-substituted phenyl)-5-carboxy uracils in different solvents. Part II.

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Absorption spectra of some 3-*N*-(4-substituted phenyl)-5-carboxy uracils, previously determined in twelve solvents, are correlated with substituent σ_p^+ values or by dual substituent parameter correlations involving σ_1 and σ_R^+ values. The substituents at the phenyl nucleus are as follows: H, Cl, Br, I, Me, Et, OMe, COOH and NO₂. Considering the structure of the investigated system, it is very probable that the effect of the substituent at the phenyl nucleus on the electronic spectra of the substituted uracils is influenced by resonance interactions between the electron pairs of both the nitrogen atoms, the carbonyl groups and the substituent itself. The polarity of the reaction medium also affects the complex resonance interactions in the molecules of the investigated compounds. The obtained results support a suggestion made by Brownlee and Topsom that UV/visible spectral shifts can conform to reasonable precise linear free energy relationships if the substituent is not a part of the chromophoric system.

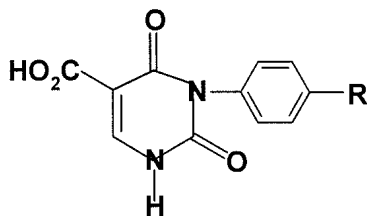
Keywords: absorption spectra, substituent effects, solvent effects, intramolecular hydrogen bond.

A number of workers¹⁻³ have reviewed and critically examined correlations of substituent constants with ultraviolet absorption frequencies. They observed that these correlations present many difficulties both in interpretation and accuracy of measurement. By means of dual substituent parameter (DSP) treatments, using various combinations of σ_R^+ , σ_R^0 , σ_R^- and σ_1 as well as $(\sigma_R^0 - \sigma_R^+)$ and $(\sigma_R^- - \sigma_R^0)$, Brownlee and Topsom^{4,5} convincingly demonstrated that previously claimed simple relationships between frequency shifts and substituent parameters were mostly unfounded when the substituents were part of the studied chromophoric system. When the substituents being varied were not part of the chromophore system, however, it was shown that good correlations were possible.

We now report further calculations which support the conclusion by Brownlee and Topsom.⁴ The system studied is 3-*N*-(4-substituted phenyl)-5-carboxy uracil

(Scheme 1). The present investigation is an extension of earlier work⁶ when the reactivities of 3-*N*-(4-substituted phenyl)-5-carboxy uracils in the reaction with diazodiphenylmethane in ethanol and methanol at 30 °C were examined using a known spectrophotometric method.⁶ These obtained kinetic data, as well as the values of the IR stretching vibrations of the carboxy carbonyl group were treated by semiempirical relationships based on the principles of linear free energy correlations. The obtained results⁶ showed that the kinetic and spectroscopic data could be well correlated with the simple and extended Hammett equation and with the Swain-Lupton equation.

We also investigated the UV spectra of the same series of compounds in twelve solvents and correlated the carboxy carbonyl transition band frequency employing the Kamlet and Taft approach⁷ using multiple regression analysis to correlate experimental data with solvatochromic parameters. The results showed that the polarity of the solvents also affects the transmission of substituent effects in 3-*N*-(4-substituted phenyl)-5-carboxy uracils.^{6,8}



Scheme 1. 3-*N*-(4-Substituted phenyl)-5-carboxy uracils
(R = H, Cl, Br, I, Me, Et, OMe, COOH, NO₂).

RESULTS AND DISCUSSION

To explain the effects of substituents in the UV spectra of 3-*N*-(4-substituted phenyl)-5-carboxy uracils,⁸ the 3-*N*-phenyl-5-carboxy uracil spectrum, which has two absorption bands one at 270–300 nm (carboxy carbonyl transition) and the other at 208–220 nm (carbonyl groups in the uracil nucleus), was taken as the reference.

The results showed that the first band is sensitive to the electronic properties of the substituent. No correlations were found for the second band.

Examination of the data given in the previous paper (Ref. 6) and the discussion presented therein shows that there is an identical trend for the ultraviolet absorption frequencies of the investigated compounds in all solvents used. The introduction of electron-donating substituents in the benzene ring produced bathochromic shifts of the long wavelength absorption maximum as compared to that of the unsubstituted uracil. Electron-attracting substituents caused hypsochromic shifts.

In order to explain these results, the absorption frequencies of carboxy carbonyl electronic transitions⁸ were correlated by the single parameter Eq. (1) using substituent s_p^+ values and by the dual substituent parameter Eq. (2) involving s_1 and s_R^+ values.

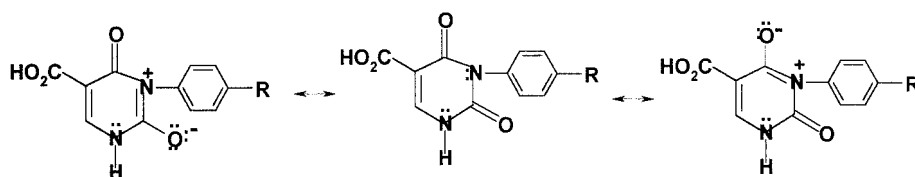
$$n = r^+ + s_p^+ + n_0 \quad (1)$$

$$n = r_I s_I + r_R s_R + n_0 \quad (2)$$

The correlations were tried with various sets of substituent parameters s , and the most satisfactory results were obtained by using s_p^+ and s_I and s_R^+ constants. The best insight into the transmission of substituent effects was obtained using the dual substituent parameter method and it was possible to distinguish between the contribution from the inductive (r_I) and the resonance (r_R^+) effects of the substituents.⁹

The values of s_p^+ , s_I , and s_R^+ are given in Table I. The results of the correlations are presented in Tables II and III. The correlation coefficients obtained from Eqs. (1) and (2) show that the data comply with a high level of reliability in all the solvents.

The composition of the electronic effect from the DSP analysis (Table III) indicates that the main effect through which these substituents influence chemical shifts of the absorption frequencies is the inductive effect, while the resonance effect is less significant. This is in agreement with the fact that the electron density at the nitrogen atom in position 3 of the carboxyuracil nucleus is influenced by both inductive and resonance effects of the *p*-substituted phenyl nucleus, which are further transmitted to the reaction center as an inductive effect. Considering that the 4-phenyl-substituted group is in the *m*-position relative to the reaction center, the total inductive effect is transmitted to the carboxy group, while the resonance effect is transmitted as a so-called secondary effect induced by the charge at the neighboring atoms in the ring. The susceptibility constants r^+ (Table II) and r_I and r_R^+ (Table III) generally decrease with decreasing solvent polarity. The blending constant 1, being defined as r_R^+/r_I , decreases simultaneously (Table III). This is attributed to the decreasing relative importance of cross-conjugation with decreasing solvent polarity. In the more polar solvents, the increased sensitivity of the investigated molecules to substituent effects is due to the greater stability of the resonance structure which, through direct conjugation, impart an enhanced resonance effect from the substituent to the reaction center. Polar solvents favor the structures shown in Scheme 2, which is also true for the reaction with DDM.⁶



Scheme 2. The structures which are favored by a polar solvent.

TABLE I. Values of substituent constants

Substituent	σ_p^{+a}	σ_I^b	σ_R^{+b}
OCH ₃	-0.78	0.27	-1.02
CH ₃	-0.31	-0.04	-0.25
C ₂ H ₅	-0.30	-0.01	-0.14
H	0.00	0.00	0.00
Cl	0.11	0.47	-0.36
Br	0.15	0.47	-0.3
I	0.14	0.40	-0.25
COOH	0.45	0.30	0.11
NO ₂	0.78	0.67	0.15

^aRef(10). ^bRef(11).

TABLE II. Results of the correlations with Eq. (1) for the 3-*N*-(4-substituted phenyl)-5-carboxy uracils

Solvents	r^+	n_0	r^a	s^b	n^c
1. Methanol	0.972	36.15	0.9753	0.106	9
2. Ethanol	0.958	36.13	0.9685	0.119	9
3. Propan-1-ol	1.202	36.07	0.9935	0.066	9
4. Propan-2-ol	0.938	36.09	0.9783	0.096	9
5. Butan-1-ol	1.111	36.02	0.9693	0.136	9
6. Dichloromethane	0.876	36.28	0.9608	0.124	8
7. Ethyl acetate	0.767	36.14	0.9767	0.082	9
8. Butyl acetate	0.918	36.18	0.9729	0.106	9
9. Chloroform	0.890	36.12	0.9603	0.125	9
10. Diethylether	1.319	36.23	0.9833	0.118	9
11. Dioxane	0.882	36.17	0.9556	0.132	9
12. Dimethylformamide	0.676	33.23	0.9689	0.084	9

^aCorrelation coefficient. ^bStandard error of the estimate. ^cNumber of points in the set.

The present study is an attempt to relate the solvent shifts of 3-*N*-(4-substituted phenyl)-5-carboxy uracils to the known properties of the solute molecule, in order to evaluate the importance of hydrogen bonding and polarization effect. The results show that there is a good correlation between the ultraviolet absorption frequencies of 3-*N*-(4-substituted phenyl)-5-carboxy uracils and the electronic properties of the substituent. The composition of the electronic effects shows the importance of the inductive effect, which is in accord with the structure of the investigated compounds.

The polarity of the solvent did not have a strong influence on the position of absorption frequencies. This is attributed to the strong intramolecular hydrogen bond in the investigated uracils, which is less significant in the more polar solvents.

It was also established here that in the more polar solvents there is an increased sensitivity of the carboxyuracil systems to substituent effects.⁸

TABLE III. Results of the correlations with Eq. (2) for the 3-*N*-(4-substituted phenyl)-5-carboxy uracils

Solvents	τ_1	τ_R^+	τ_R^+/τ_1	n_0	r^a	s^b	n^c
1. Methanol	1.020	0.999	0.979	36.12	0.9780	0.109	9
2. Ethanol	0.907	1.026	1.131	36.14	0.9643	0.137	9
3. Propan-1-ol	1.273	1.194	0.937	36.01	0.9783	0.131	9
4. Propan-2-ol	1.065	0.892	0.837	36.02	0.9647	0.132	9
5. Butan-1-ol	1.413	0.975	0.690	35.88	0.9675	0.152	9
6. Dichloromethane	1.132	0.739	0.652	36.14	0.9792	0.099	8
7. Ethyl acetate	0.883	0.727	0.823	36.08	0.9666	0.105	9
8. Butyl acetate	1.040	0.868	0.834	36.12	0.9555	0.146	9
9. Chloroform	1.177	0.769	0.849	35.99	0.9714	0.115	9
10. Diethylether	1.591	1.213	0.762	36.10	0.9786	0.144	9
11. Dioxane	1.058	0.830	0.784	36.09	0.9604	0.134	9
12. Dimethylformamide	0.826	0.635	0.768	33.16	0.9806	0.071	9

^aMultiple correlation coefficient. ^bStandard error of the estimate. ^cNumber of points in the set.

The fact that the correlations of the ultraviolet absorption frequencies of 3-*N*-(4-substituted phenyl)-5-carboxy uracils by Eq. (1) and Eq. (2) were satisfactory indicates the correct selection of the models used. This means that these models give a correct interpretation of the transmission of the electronic effect in the complex system of the 3-*N*-(4-substituted phenyl)-5-carboxy uracils nucleus. The results obtained in this work support the suggestion by Brownlee and Topsom that UV/visible spectral shifts can conform to reasonably precise linear free energy relationships if the substituent does not interact strongly with the chromophore system.⁴

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ИЗВОД

ЕФЕКАТ СУПСТИТУЕНАТА НА АПСОРПЦИОНЕ СПЕКТРЕ 3-*N*-(4-СУПСТИТУИСАНИХ ФЕНИЛ)-5-КАРБОКСИ УРАЦИЛА У РАЗЛИЧИТИМ РАСТВОРАЧИМА. ДЕО II.

Н. ВАЛЕНТИЋ, Г. УШЋУМЛИЋ И М. РАДОЈКОВИЋ-ВЕЛИЧКОВИЋ
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Апсорпциони спектри 3-*N*-(4-супституисаних фенил)-5-карбокси урацила (супституенти: H, Cl, Br, I, Me, Et, OMe, COOH и NO₂) су корелисани простом и проширеном Hammett-овом једначином укључујући s_p^+ односно s_1 и s_R^+ константе у дванаест растварача различите поларности. Задовољавајући резултати корелације апсорпционих спектра за електронске прелазе у карбокси карбонилној групи са константама супсти-

уената су потврда исправности одабраног модела за проучавање механизма преношења ефеката супституената кроз сложене молекуле 3-*N*-(4-супституисаних фенил)-5-карбоксии урацила.

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