

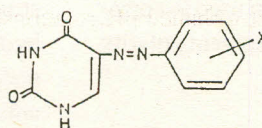
ELECTRONIC SPECTRAL PROPERTIES OF SUBSTITUTED AZOURACIL COMPOUNDS

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Synthesis of 5-(substituted phenylazo) uracil compounds (I) have been reported. The analytical data and $^1\text{H-NMR}$ are used to elucidate the structures. The electronic spectral properties of the organic compounds were investigated in presence of different solvents and at different pH's. The pK's values were determined and related with the molecular structure of the compounds. The electronic transitions were assigned. The phenomenon of tautomerism was explained. The shifts in peak locations in the electronic spectra of the organic compounds have been correlated with different solvent polarity parameters.



X = -H; 2-CH₃; 3-CH₃; 3-OH; 2-COOH; 4-COOH; 2-Cl; 3-Cl; 4-Cl; 2-Br; 3-NO₂; 2,5-diCH₃; 2,5-diCl and 2,4-diCl.

Key words: Electronic spectra, Azo compounds, Uracil compounds.

Introduction

Azo compounds are by far the most important class of dyes comprising over 50% of total world dye stuffs production (Patai 1975). The formation of metal complexes has figured prominently in dye stuff chemistry from very early times. The azo group is connected with a number of important biological reactions such as protein synthesis (Tu *et al* 1974), inhibition of carcinogenesis (Rosenberg 1971), immunochemical affinity and nitrogen fixation (Eichhorn 1973). The pyrimidine compounds are important class of compounds for their structural chemistry and biological activities.

In our laboratory (Vogel 1961; Masoud *et al* 1991; Masoud *et al* 1992 a,b,c; Khalil *et al* 1993; Masoud *et al* 1994 a,b,c), a series of papers have been published about the structural chemistry of the pyrimidine compounds especially those containing azo group.

In the present paper, the electronic spectra of 5-(substituted phenylazo) uracil compounds in different organic solvents and at different pH's have been analyzed. The major objective of such work lies in the following:

(i) Evaluation of the pK's values and their interpreting them in relation to the molecular structure of the compounds, (ii) the assignment of the electronic transition, (iii) explaining the phenomena of tautomerism, (iv) illustrating the type of hydrogen bonding, (v) the shift in the peak position is correlated to

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different solvent polarity parameters using the multiple linear regression technique.

Experimental

The 5-(Substituted phenylazo) uracil compounds containing groups with different electronic properties (-H, 2-CH₃; 3-CH₃; 3-OH; 2-COOH; 4-COOH; 2-Cl; 3-Cl; 4-Cl; 2-Br; 3-NO₂; 2,5-diCH₃; 2,5-diCl and 2,4-diCl) were prepared by usual method of diazotization of phenolic compounds (Vogel 1961). The compounds (I) were characterized by their elemental analysis given in Table 1.

$^1\text{H-NMR}$ of the organic compounds in presence of $d^6\text{-DMSO}$ or $d^1\text{-HCCl}_3$ were recorded on Varain EM-Model 3930-90 MHz Spectrometer. Tetramethylsilane (TMS) was used as an internal standard.

The electronic spectra were recorded using Pye Unicam SP 1800 Spectrophotometer at different pH's (1.03-10.80) and in the presence of different solvents.

Universal buffer solutions were prepared as usual. Dioxane and ethanol solvents were purchased from BDH and Merck companies and were purified following published methods. The other solvents, (cyclohexane, chloroform, carbontetrachloride, DMF, DMSO, acetonitrile, acetone, aq. NH₃ and ether) were of spectroquality grade.

Method of Calculations. The observed peak location of an absorption band Y in a given solvent has been expressed as a

linear function of different solvent polarity parameters $x_1, x_2, x_3, \dots, x_n$ as follows:

$$Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + \dots + a_nx_n \dots (i)$$

This equation is amendable to solution for the intercept a_0 and the coefficients a_1, a_2, \dots, a_n by multiple regression. The multiple regression (R) or (MCC) and the probability of variation (P), which are calculated from the modified SPSS programme, have been considered as a measure of the goodness of the fit. The regression intercept a_0 has been considered as the peak position in the gas phase spectra. Several one, two three and four-parameters equations have been used to correlate the spectral shifts with various empirical solvent polarity parameters which are

$$E = 2.859 \times 10^{-3} \nu \dots (ii)$$

$$K = (D-1)/(2D+1) \dots (iii)$$

$$M = (n^2-1)/(2n^2+1) \dots (iv)$$

$$J = (D-1)/(D+2) \dots (v)$$

$$H = (n^2-1)/(n^2+2) \dots (vi)$$

$$N = J - H \dots (vii)$$

The parameter E given by equation (ii) is related to ν which is the wave number of the absorption maximum (Masoud *et al* 1993). This function is sensitive to both solvent-solute hydrogen bonding and dipolar interactions. The dielectric function K adequately represents the dipolar interactions and is related to the dielectric constant (D) of the solvent (Masoud *et al* 1993). The functions J and H have been introduced to account for the non-specific solute-solvent interactions such as dispersion and dipolar effects (Masoud *et al* 1993). These are related to the dielectric constant and refractive index (n) of the solvents, respectively. The functions M and N have been introduced to account for the solute permanent dipole-solvent induced dipole and solute permanent dipole-solvent permanent dipole interactions, respectively (Hillard *et al* 1981).

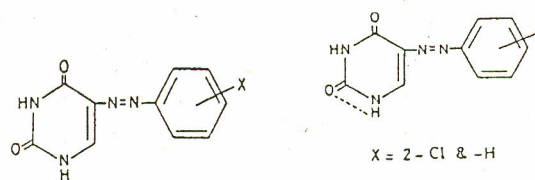
Results and Discussion

a) NMR Spectroscopy. The ^1H NMR spectra of uracil and its 5-substituted arylazo compounds are present in Table 2.

1) The multiple signals in the range 6.9-8.0 ppm are assigned for phenyl protons with total number of 4 protons except the phenylazouracil and 2, 4-dichloro compounds where the number of protons is 5 and 3, respectively. (2) A doublet signal at 5.3-5.5 ppm is due to 2 CH for uracil and 1 CH for its phenylazo derivatives. (3) A sharp doublet signal at 3.9-4.1 ppm is due to $-\text{OCH}_3$ group. (4) The doublet broad signal at 6.7-6.9 ppm is assigned for the protons of the $-\text{COOH}$ group

attached to the phenyl ring. (5) The hydroxy group gave a broad signal at 8.6-8.9 ppm for the 3-hydroxy compound, probably in a dimeric structure. (6) The broad band at 10.4-11.1 ppm is due to NH group to assign the presence of the keto group. This band is absent in compounds containing-H, 2-OCH₃, and 2-Cl substituents, probably due to strong solute solvent interaction. (7) The presence of doublet signals at 7.4-7.6 ppm and 7.8-8.0 ppm in 2-COOH and 4-COOH substituted arylazo compounds, respectively are related to the presence of intramolecular hydrogen bond. (8) The signals 7.7-7.9 and 8.7-8.9 ppm for the parent phenylazo and its 2-Cl substituent, respectively are due to NH...O hydrogen bonded structure. (9) In general, the strength of the intramolecular hydrogen bond of the NH...O type is greatly influenced by the nature of the substituent. The electron withdrawing substituents decrease the intramolecular hydrogen bond to a great extent as indicated by the strong shift of the -OH signal. The electron donating substituents show the presence of intramolecular hydrogen bond of the NH...O due to the increasing basicity of the azo nitrogen.

The following possible structures are given:



$X = 3\text{-OH}, 2\text{-}, 4\text{-COOH}, 2\text{-OCH}_3$ (in CDCl_3) & $2,4\text{-diCl}$

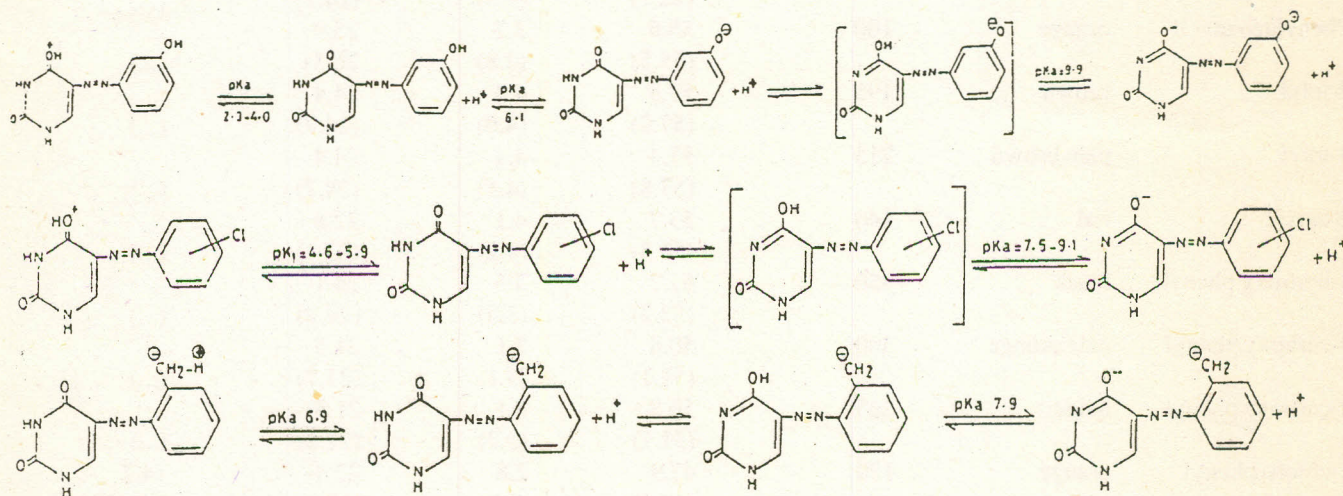
(b) Electronic Spectroscopy. The effect of pH on the electronic absorption spectra of the organic compounds gave different λ_{max} with some isobestic points. For uracil, two characteristic bands at 208 and 258 nm are due to $\pi\text{-}\pi^*$ transition.

The second is vanished in solutions with $\text{pH} > 9$ with the existence of a new band at 285 nm, due to the existence of an intramolecular hydrogen bond between (N(3)H & N(1)H) with $2\text{C}=\text{O}$. The first band assigned to the increase of the aromatic character of uracil ring.

On comparing the electron absorption spectra of the azo compounds to that of uracil, more bands are observed. Two $\pi\text{-}\pi^*$ transition bands are observed at (234 up to 250) and (260 up to 286) nm, due to the shift of the tautomeric equilibrium towards the enol form in moderately basic solutions. The band at 350nm is due to $n\text{-}\pi^*$ transition of CT nature of the azo group as a donor site, while that at 430-450 nm is due to the existence of azo \rightarrow hydrazo equilibrium.

Different positions are available for protonation -NH, C=O and N=N to give $^+NH_2$, $C=O^+H$ and $N=N^+H$, respectively. The proton is bound symmetrically to both N atoms, i.e., acts as a single basic site or the proton is bound to the azo group in the form of π -complex. The azo group can act as a proton acceptor in hydrogen bonds. The aromatic azo compounds are resonance stabilized and tautomerism involving the azo group is well known (Jaffe 1953). The new band recorded for 2-OCH₃ compound at 530 nm, is probably due to the existence of hydrazo structure. However, for the 3-OH compound, the absence of 250 nm band argued the slight contribution of the enol tautomer beside the protonated species.

For the absorbance-pH relationships, the half-height (Issa 1971) and the modified limiting absorption (Muk and Pravica 1969) methods to evaluate the pK_a values gave concordant results (Table 3). All the compounds gave one pK_a in the range 6.9-9.7 due to the ionization of -OH group, except the 2-OCH₃; 3-OH; 2-COOH; 2-Cl; 3-Cl; 4-Cl; 2-Br; 4-COOH; 2,5-diCH₃ and 2,4-diCl compounds which gave more than one pK_a , due to the ionization of the two -OH groups.



The pK_a of uracil is higher than that of phenylazouracil, due to the basicity of the azo group with the presence of different tautomeric structures. Also, the low pK_a of 2-CH₃ is probably explained on the basis that the -CH₃ group exists in a structure $-CH_2H^+$. The pK_a of 2-OCH₃ is smaller than that of uracil but higher than that of 2-CH₃, probably due to the bulkiness of -OCH₃ group with the possible existence of different tautomeric forms. The pK_a of 2-OCH₃ (5.6) is due to the ionization of the $-OCH_2H^+$ group. The value of pK_a of 2-OCH₃ in non-buffered media (9.4) is higher than that deduced in buffered media (8.2), probably due to the buffer, that may be form some molecular complexes. The pK_a of 3-OH compound (6.1) is

due to the ionization of the phenolic -OH group. However, the pK_a of 4-COOH and 2-COOH compounds are 5.4 and 7.0, respectively due to the ionization of the carboxy group (Masoud *et al* 1985). The unexpected high pK_a (7.0) of ionization of -COOH group suggests the formation of strong intramolecular H-bond, i.e., the carboxy behaves as an electron donor since it ionized through its resonating structure (Masoud *et al* 1985). The pK_2 values are in the order 4-Cl > 2-Cl > 3-Cl, and correlated to the position and the electronic character of the substituents. The lower pK_a values of 2- and 3-Cl substituents compounds than that of uracil are due to the electron attracting property of chlorophenylazo group. The $pK_{Br} > pK_{Cl}$ is due to the high electronegativity of -Cl atom.

The higher pK_a of 2,5-diCH₃ compound than that of 2-CH₃ compound, is due to the hyperconjugation and the basicity of the two -CH₃ groups. The dichloro compounds are with higher pK_a values due to the electron attracting property of the two -Cl groups. The pK_a of 2,5-diCl is higher than that of 2,4-diCl. The mechanism of ionization of some compounds is given as follows:

However, the electronic spectral data of the organic compounds are affected by the solvents of variable polarities (Table 5). The data showed that uracil gave $\pi-\pi^*$ transition band at 254 nm which is red shifted with the decrease of the dielectric constant of the solvent. So, the solute molecule can act as the hydrogen donor in forming the hydrogen bond. This band is splitted in aq. NH₃ and ether to 256, 282 & 260, 286 nm, respectively. (The band at 282-286 nm appeared in buffered media at pH>9). Another $\pi-\pi^*$ transition band at 234 nm in ether has appeared and blue shifted with more polar hydrogen donor solvent, due to the presence of solute-solvent interaction through hydrogen bond formation. The new band at 330

and 334 nm in ether and acetone, respectively, has appeared with low intensity, due to the forbidden $n-\pi^*$ electronic transition of an electron from a lone pair orbital of N or O to the π -orbital of the ring system.

For phenylazouracil compound, a well defined band is appeared at 350 nm, due to the $n-\pi^*$ electronic transition of CT nature with the azo group as a donor, i.e., solute solvent interaction exists. The extra $n-\pi^*$ electronic transition in the wavelength range 286-294 nm is present in all solvents used, except in presence of acetone. On the other hand, the $\pi-\pi^*$ electronic transition at 234 nm is red shifted with the decrease of the dielectric constant of the solvent (similar to uracil), due to conjugation. The bands at 450 and 500 nm in CCl_4 and

aq. NH_3 , respectively, are probably assigned the hydrazo structure (Basu Baul *et al* 1983).

The spectra of 2- CH_3 compound is strongly similar to that of 3- CH_3 and 2- OCH_3 compounds. Three $\pi-\pi^*$ electronic transitions are detected at 288-300, 230-246 and 210-220 nm, and are assigned to the transition of the phenyl ring overlapped by a composite broad $\pi-\pi^*$ of the azo structure (Masoud and Khalil 1991). The spectra gave a characteristic $n-\pi^*$ transition band at 350 nm which is red shifted in presence of CCl_4 , CHCl_3 , DMF, DMSO and aq. NH_3 solvents. This points to solute-solvent interaction (Masoud and Haggag 1982), especially in aq. NH_3 where the red shift is high. The band at 430-470 nm is appeared in all solvents used except DMF, probably

Table 1
m.p. colour and analytical data of the organic compounds

Compound	Colour	m.p. °C	Calculated/(found) %			
			C	H	N	X
Uracil	white	338	42.8 (42.7)	3.6 (3.5)	25.0 (24.7)	... (...)
Phenylazo uracil	orange	100	55.6 (55.5)	3.7 (3.8)	25.9 (26.3)	... (...)
2-tolyl	brown	195	57.4 (57.7)	4.4 (4.6)	24.4 (24.7)	... (...)
3-tolyl	pale brown	215	57.4 (57.8)	4.4 (4.6)	24.4 (24.7)	... (...)
2-anisyl	red	140	53.7 (53.5)	4.1 (4.2)	22.8 (23.1)	... (...)
3-hydroxy phenyl	black	350	51.7 (52.2)	3.5 (3.5)	24.1 (24.2)	... (...)
4-carboxy phenyl	pale orange	300	50.8 (51.1)	3.1 (3.1)	21.5 (21.7)	... (...)
2-carboxy phenyl	beige	265	50.8 (51.1)	3.1 (3.2)	21.5 (21.8)	... (...)
2-chloro phenyl	orange	130	47.9 (48.0)	2.8 (2.9)	22.4 (22.6)	14.2 (14.5)
3-chloro phenyl	deep orange	93	47.9 (47.9)	2.8 (2.8)	22.4 (22.5)	14.2 (14.2)
4-chloro phenyl	reddish brown	215	47.9 (47.5)	2.8 (2.9)	22.4 (22.7)	14.2 (14.3)
2-bromo phenyl	reddish brown	95	40.7 (40.7)	2.4 (2.5)	19.0 (19.4)	27.1 (27.4)
3-nitro phenyl	yellow	186	46.0 (45.9)	2.7 (2.9)	26.8 (27.2)	... (...)
2,5-dimethyl	pale grey	275	59.0 (59.5)	4.9 (5.0)	23.0 (23.2)	... (...)
2,5-dichloro	brown	130	42.1 (40.5)	2.1 (2.3)	19.7 (20.2)	24.9 (24.5)
2,4-dichloro	beige	160	42.1 (40.4)	2.1 (2.3)	19.7 (20.2)	24.9 (24.5)

due to hydrazo formation. Beside such finding, there is a band at 530-534 nm in 2-OCH₃ compound, probably due to the difference in the basicity between -CH₃ and -OCH₃ groups.

In 3-OH compound, n- π^* electronic transition is assigned in the range 358-372 nm in ethanol, acetone and aq. NH₃

Table 2
¹H-NMR spectral data (δ , ppm) for uracils

Compound	Signals (δ , pp)	Assignment
Uracil	5.3 - 5.5 (doublet)	C - H
	7.2 - 7.4 (doublet)	
	10.4 - 11.1 (broad)	NH
5-phenylazouracil	6.6 - 6.8 (broad)	C - H
	6.9 - 7.5 (multiplet)	C ₆ H ₅
	7.7 - 7.9 (broad)	NH...0
2-anisylazouracil (DMSO)	3.9 - 4.1 (doublet)	OCH ₃
	6.8 - 7.6 (multiplet)	C ₆ H ₄
	7.7 - 8.0 (triplet)	C - H
	8.8 - 8.9	
2-anisylazouracil (CDCl ₃)	3.9 - 4.1	OCH ₃
	6.8 - 7.5 (multiplet)	C ₆ H ₄
	7.7 - 7.9 (doublet)	C - H
	9.1 - 9.4 (triplet)	
3-hydroxyphenyl- azouracil	10.7 - 11.0 (doublet)	NH
	3.7 - 3.8	
	5.3 - 5.5 (doublet)	C - H
	7.1 - 7.4 (multiplet)	C ₆ H ₄
	8.6 - 8.9 (broad doublet)	OH phenolic
2-carboxyphenyl- azouracil	10.5 - 11.1	NH
	5.3 - 5.5 (doublet)	C - H
	6.7 - 6.9	H of COOH
	7.2 - 7.6	C ₆ H ₄
	10.5-11.1 (doublet broad)	NH
4-carboxyphenyl- azouracil	5.3 - 5.5 (doublet)	C - H
	6.7 - 6.9 (doublet)	H of COOH
	7.2 - 8.0 (multiplet)	C ₆ H ₄
	10.4 - 11.3 (broad)	NH
2-chlorophenyl- azouracil	4.7 - 4.8	
	5.2 - 5.3	
	5.5 - 5.7 (doublet)	C - H
	7.2 - 8.0 (multiplet)	C ₆ H ₄
2,4-dichlorophenyl- azouracil	8.7 - 8.9	NH...0
	5.3 - 5.5 (doublet)	C - H
	7.2 - 7.8 (multiplet)	C ₆ H ₃
	10.5 - 11.2 (doublet broad)	NH

solvents of a broad nature. It is absent in the other solvents. Since the -OH group is of a strong donor property, this band is assigned to be of intramolecular charge transfer behaviour. The band is red shifted in more polar solvents, due to more stabilization of excited state than ground state (Hasanein *et al* 1988). The disappearance of the n- π^* transition for the azo group in 2-COOH compound is probably due to the intramolecular hydrogen bond mainly between the carboxy and the azo groups (Alexander and Sleet 1970; Masoud and Khalil 1991; Masoud *et al* 1995), beside the steric effect of the 2-carboxy group. The π - π^* transition at 206-230 nm in presence of hydrogen bonding solvents (e.g. ethanol, aq. NH₃ and ether) is due to the presence of an external hydrogen bond affected through K band (Dearden and Forbes 1960). In 4-COOH compound, the n- π^* transition of the azo group, is detected with no hydrogen bond between the -COOH and -N=N-groups. The π - π^* electronic transition bands of the 2-COOH compound are of great similarity to that of the 4-COOH compound.

In case of 2-Cl compound, the n- π^* of the azo group is appeared at longer wavelength than that of 5-(phenylazo) compound,

Table 3
pKa values of the organic compounds spectrophotometrically (25°C, 0.5M - KCl)

Compound	Half height	Modifying limiting absorption
uracil	9.0	8.9 λ 258 nm
-H	6.9	6.9 λ 370 nm
2-CH ₃	6.7	6.6 λ 250 nm
	7.9	7.9 λ 350 nm
2-OCH ₃	8.2	8.3 λ 470 nm
	5.6, 8.2	5.6, 8.3 λ 242 nm
2-OCH ₃ (DMF)	9.4	9.4 λ 468 nm
3-OH	2.3, 6.1, 9.9	2.3, 6.1, 10.0 λ 430 nm
	2.4, 4.0	2.4, 3.9 λ 222 nm
4-COOH	5.4	5.4 λ 358 nm
	9.3	9.3 λ 258 nm
2-COOH	9.0	9.0 λ 230 nm
2-COOH(DMF)	2.2, 7.0	2.1, 7.1 λ 370 nm
2-Cl	4.6, 8.6	4.6, 8.6 λ 370 nm
3-Cl	5.9, 7.5	5.9, 7.6 λ 290
4-Cl	4.9, 9.1	5.0, 9.2 λ 250 nm
2-Br	5.7, 9.3	5.7, 9.3 λ 230 nm
	5.4, 7.7	5.4, 7.8 λ 250 nm
2,5-diCH ₃	9.2	9.2 λ 390 nm
	2.3, 6.6, 8.7	2.3, 6.7, 8.6 λ 370 nm
2,5-diCl	9.7	9.6 λ 358 nm

due to the electron attracting property of the chloro group. In a similar scope of investigation, no dramatic changes are observed between the electronic absorption spectra of the 2-Cl and both 3-Cl and 4-Cl derivatives. However, the λ_{\max} of the 2-Cl compound is at a lower position compared to both 3- and 4-Cl compounds. Also, the electronic spectral features of the 2-bromo compound are of great similarity to the 3-Cl compound. For the nitro compound, with the strong attracting property of the nitro group, the 3-nitro compound absorbs at a lower position than the chloro compounds.

In general, the arylazo group is sufficiently polar for proximity effects to become significant in the orthoposition. The tautomeric equilibrium controlled by the intensity of the spectral bands, is high in presence of basic solvents than in a alcohol. The electronic effect of the aryl group is transmitted through the azo group and the phenyl ring.

In 2,4- and 2,5-diCl compounds, more chlorine leads to red shift of the electronic spectral bands with increasing the dielectric constant of the solvents (D). The $n-\pi^*$ band of the 2,4-diCl compound absorbs at a slightly lower λ_{\max} than that of the 2,5-diCl compound. The hydrazone species at 410-520 nm is detected in presence of cyclohexane, DMF, DMSO, aq. NH_3 , acetone and CCl_4 solvents and located at a higher λ_{\max} than the 2-Cl compound, due to the presence of more electron attracting property of the two chloro groups. However, the 2,5-di- CH_3 compound absorbs at a longer λ_{\max} than either 2- or 3-tolyl, 2,5-diCl and 2,4-diCl compounds, due to the hyper-

conjugation effect of the two $-\text{CH}_3$ groups.

(c) *Computer Analysis.* The results of calculations for the organic compounds under investigation are collected in Tables (4,6-9). For the uracil and its phenylazo compounds, the solvent spectral regions are

($Y_1=232-268$, $Y_2=270-308$, $Y_3=322-390$ & $Y_4=430-458$ nm).

Based on one parameter equation, the followings are observed:

(1) For Y_1 and Y_3 , the best correlation for the compounds, among these single solvent polarity parameters has been obtained with M. So, the solute permanent dipole solvent induced dipole interaction is the most effective on the spectral shifts from the one parameter equation view. (2) Based on Y_2 , the four parameters are poorly effective. But N & K are more effective than M & E. (3) In spite of E, N & K are the most effective parameters based on Y_4 (due to hydrazo \rightarrow azo) spectral analysis, the parameter E is the power. This indicated that, the spectral shifts of visible band Y_4 are highly sensitive to solute-solvent H-bonding and the (D).

For two-parameters equations, we showed that: (1) The spectral analysis derived from Y_1 , Y_2 & Y_3 bands showed that the combinations of the parameter M with N, K or E parameters are the most effective. (2) The combinations of E with N and K are less effective than that with M, i.e., the solute-solvent

Table 4
Different calculated regression coefficients for Y_1 of uracil

Parameters $X_1X_2X_3X_4$	Y_1 a_0	a_1	a_2	a_3	a_4	MCC	P
E	259.960	-0.325				0.045	0.915
N	255.067	6.735				0.269	0.519
M	226.769	164.517				0.464	0.246
K	249.229	22.307				0.331	0.424
E K	256.309	-0.419	50.623			0.524	0.448
E N	269.250	-0.455	19.003			0.483	0.515
E M	213.945	0.146	196.898			0.499	0.489
N M	211.835	11.235	212.266			0.632	0.280
N K	206.566	-71.129	212.148			0.524	0.448
M K	208.237	196.240	29.867			0.635	0.275
E M K	218.743	-0.213	163.114	42.937		0.662	0.466
E N K	227.510	-0.257	-43.430	155.538		0.558	0.647
E N M	225.896	-0.255	17.494	182.355		0.666	0.458
E N M K	227.949	-0.265	22.602	188.216	-12.845	0.666	0.691

Table 5
Solvent effects on the electronic absorption spectra of the organic compounds (λ_{\max} , nm)

Compound	Cyclohexane	Dioxane	CCl ₄	Other	HCCl ₃	Acetone	Ethanol	DMF	Acetonitrile	DMSO	Aq. NH ₃	H ₂ O
Uracil	--	254	--	234,260 286,330	254	344	206 258	270	216 250	266	222,256 282	202 256
-H	234,290 350	238,292 354	260,330 450	236,288 350	240,286 350	350	234,288 350	294 356	238,292 350	294 358	290,354 500	--
2-CH ₃	210,244 350,430	244,350 440	352 440	230,348 440	244,354 450	350 440	204,232 300,350 450	265 354	246,350 444	265,354 458	220,246 286,374 450	--
3-CH ₃	215,237 352,455	351 461	258,356 448	206,238 352,448	246,353 455	349 455	214,238 327,358 445	267,361 463	240,348 455	261,359 461	222,285 372,445	--
2-OCH ₃	246,283 450	240,298 362,450	254,298 450,530	234,286 340,460	244,308 466,530	340,470 530	210,302 470,530	270,300 470	222,246 302,466 534	262,300 470,530	226,266 278,468	--
3-OH	--	254	--	236,284 436	246	358 432	206,246 364,442	264 430	252	265,400 446	222,282 372,456	--
2-COOH	--	253,306 352	270,310 346,400	230,256 282	244,304 430	348,418 448	206,256 300	265,298	252,294 428	264 294	224,283 386	--
4-COOH	--	254 370	264,284 320	250,354 430	256 366	365	210,258 370	266 374	250 362	265 378	268 280	--
2-Cl	214,230 290	234,282 354,430	298 420	213,290 364,452	244,302 368,450	356	206,242 290,360 450	265 368	246,298 358,442	270,362 450	234,284 390,532	--
3-Cl	214,240 300,352	245 354	262 364	210,239 353	244 356	357	208 353	267 360	244 350	262 363	223,285 389	--
4-Cl	216,250 330,360 430	240,305 438	260,330 428	232,290 340	246,348 450	330 440	205,242 342	256,340 450	250,336 456	266,340 440	234,258 268,288 374,448	--

(Cont'd.....)

2-Br	214,250	245,352	264,297	209	234	205,218	212	268	227	261	223,285	--
	290,340		355	347	355	348	349	352	348	352	386	
3-NO ₂	--	235,270	260	232	240,266	338	220,242	270	252	278	236,256	--
		330	326	320	328		270,322	330		334	264,274	
2.5-diCH ₃	216,249	250	368	234,284	248	366	208,254	264,366	250,366	264,302	256,264	--
	364,450	366	478	364	366	460	366	470	468	370,470	284,420	
2.5-diCl	216,246	240	230,294	232,282	245,299	205,218	210,240	270,300	246,300	262,302	228,292	--
	290,360	358	362,470	352	364	355,508	296,358	362,440	358	362,440	410	
2.4-diCl	214,247	246	260,300	226,240	250,300	358	208,250	266,306	248,300	264,304	264,284	--
	304,362	360	356	294,360	362		306	362,520	356	362,520	384	
	450							490		490		

Table 6
Different calculated regression coefficients for Y₁, Y₂, Y₄ & Y₅ of 5-(anisylazo)uracil

Parameters X ₁ X ₂ X ₃ X ₄	Y ₁							Y ₂						
	a ₀	a ₁	a ₂	a ₃	a ₄	MCC	P	a ₀	a ₁	a ₂	a ₃	a ₄	MCC	P
E	224.646	0.580				0.372	0.411	265.496	0.900				0.390	0.265
N	243.899	9.385				0.310	0.499	292.237	23.824				0.473	0.168
M	174.642	385.112				0.696	0.082	343.866	-213.930				0.236	0.512
K	238.692	23.918				0.316	0.491	278.866	61.366				0.479	0.162
EK	216.599	0.969	-20.170			0.383	0.728	287.385	-0.390	80.617			0.485	0.392
EN	203.338	1.092	-10.560			0.390	0.719	305.482	-0.408	31.824			0.479	0.401
EM	140.538	0.735	389.727			0.838	0.089	290.257	0.808	-106.949			0.405	0.533
NM	153.548	16.773	439.353			0.875	0.055	302.199	22.738	-48.356			0.475	0.408
NK	234.875	-7.167	41.700			0.317	0.809	271.025	-14.403	97.814			0.480	0.401
MK	150.518	416.217	37.802			0.849	0.078	293.912	-69.792	57.898			0.484	0.393
EMK	148.164	0.140	412.244	31.292		0.849	0.228	303.851	-0.411	-74.200	77.991		0.491	0.620
ENK	202.199	1.075	-22.533	30.957		0.393	0.901	284.784	-0.377	-4.271	90.800		0.485	0.630
ENM	167.212	-0.610	28.426	469.545		0.833	0.163	313.954	0.393	30.554	-43.484		0.481	0.637
ENMK	211.459	-0.943	149.038	604.681	-282.845	0.968	0.121	290.040	-0.312	-37.658	-115.330	166.317	0.495	0.799

(Contd...)

$X_1X_2X_3X_4$	Y_4						Y_5							
	a_0	a_1	a_2	a_3	a_4	MCC	P	a_0	a_1	a_2	a_3	a_4	MCC	P
E	416.300	1.141				0.849	0.002	528.142	0.059				0.239	0.649
N	451.215	27.654				0.943	0.000	529.605	2.136				0.371	0.469
M	491.557	-148.945				0.282	0.430	538.930	-41.945				0.526	0.284
K	435.335	72.200				0.967	0.0001	528.667	4.841				0.312	0.547
EK	436.808	-0.067	75.529			0.968	0.000	529.391	-0.036	6.816			0.320	0.851
EN	450.516	0.022	27.232			0.943	0.001	532.788	-0.098	4.137			0.416	0.753
EM	415.767	1.143	2.301			0.849	0.114	540.731	-0.023	-46.142			0.532	0.608
NM	438.305	29.060	62.664			0.949	0.0003	537.899	0.480	-37.923			0.530	0.609
NK	407.569	-51.005	201.269			0.985	0.000	541.812	21.621	-53.001			0.574	0.549
MK	427.758	35.145	73.946			0.964	0.0001	538.260	-40.022	0.705			0.528	0.613
EMK	429.146	-0.05	34.530	76.752		0.970	0.001	541.403	-0.099	-44.800	5.664		0.560	0.824
ENK	404.251	0.091	-53.449	202.960		0.985	0.0001	544.810	-0.094	23.434	-52.677		0.602	0.782
ENM	438.307	-0.00005	29.061	62.665		0.949	0.002	542.291	-0.119	2.819	-40.253		0.577	0.808
ENMK	405.840	0.111	-63.544	-34.875	225.796	0.986	0.0004	545.760	-0.106	16.970	-19.405	-36.765	0.618	0.936

Table 7

Calculated regression coefficients for phenylazouracil compound and its 2-tolyl derivative

Parameters $X_1X_2X_3X_4$	Y_1 (-H)		Y_2 (-H)		Y_3 (-H)		Y_1 (2-CH ₃)		Y_3 (2-CH ₃)		Y_4 (2-CH ₃)	
	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P
E	0.364	0.422	0.181	0.668	0.434	0.210	0.179	0.672	0.191	0.598	0.703	0.035
N	0.387	0.391	0.328	0.427	0.478	0.163	0.352	0.393	0.186	0.607	0.626	0.072
M	0.576	0.176	0.314	0.449	0.088	0.809	0.695	0.056	0.758	0.011	0.230	0.553
K	0.366	0.419	0.286	0.493	0.483	0.157	0.370	0.367	0.251	0.485	0.687	0.041
EK	0.374	0.740	0.321	0.762	0.483	0.394	0.481	0.518	0.260	0.782	0.716	0.116
EN	0.388	0.721	0.412	0.627	0.478	0.404	0.463	0.548	0.194	0.875	0.703	0.129
EM	0.576	0.446	0.403	0.642	0.438	0.474	0.770	0.105	0.893	0.004	0.881	0.011
NM	0.589	0.426	0.514	0.465	0.491	0.381	0.865	0.032	0.929	0.001	0.867	0.015
NK	0.416	0.685	0.472	0.533	0.484	0.392	0.393	0.657	0.652	0.144	0.857	0.019
MK	0.587	0.429	0.462	0.549	0.491	0.380	0.847	0.042	0.938	0.001	0.894	0.008
EMK	0.621	0.644	0.471	0.774	0.491	0.618	0.869	0.103	0.938	0.004	0.916	0.020
ENK	0.416	0.885	0.560	0.643	0.485	0.631	0.482	0.760	0.660	0.297	0.930	0.013
ENM	0.647	0.603	0.565	0.635	0.491	0.619	0.908	0.055	0.929	0.005	0.899	0.030
ENMK	0.667	0.802	0.884	0.223	0.492	0.803	0.962	0.049	0.946	0.012	0.970	0.010

Table 8

Calculated regressions coefficients for 3-chloro; 2,4-dichloro; 2,5-dichloro; 2-chloro; 2-bromo and 3-hydroxyphenylazouracil compounds

Parameters $X_1X_2X_3X_4$	$Y_1(3\text{-Cl})$		$Y_3(3\text{-Cl})$		$Y_1(2,4\text{-diCl})$		$Y_3(2,5\text{-diCl})$		$Y_1(2,5\text{-diCl})$		$Y_2(2,5\text{-diCl})$		$Y_3(2,5\text{-diCl})$	
	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P
E	0.339	0.338	0.071	0.845	0.280	0.466	0.021	0.958	0.437	0.240	0.537	0.136	0.025	0.946
N	0.203	0.574	0.001	0.998	0.349	0.358	0.039	0.920	0.580	0.101	0.416	0.265	0.105	0.772
M	0.700	0.024	0.715	0.020	0.647	0.060	0.452	0.222	0.332	0.382	0.390	0.299	0.807	0.005
K	0.169	0.641	0.050	0.892	0.372	0.325	0.011	0.978	0.590	0.094	0.424	0.255	0.062	0.866
EK	0.445	0.461	0.257	0.788	0.392	0.606	0.093	0.975	0.628	0.222	0.553	0.334	0.184	0.886
EN	0.409	0.527	0.164	0.909	0.361	0.658	0.064	0.988	0.622	0.231	0.565	0.315	0.290	0.735
EM	0.708	0.087	0.738	0.064	0.828	0.031	0.456	0.497	0.664	0.175	0.801	0.046	0.866	0.008
NM	0.705	0.090	0.783	0.036	0.884	0.010	0.467	0.477	0.807	0.042	0.701	0.132	0.843	0.013
NK	0.374	0.590	0.464	0.429	0.418	0.562	0.465	0.482	0.593	0.272	0.427	0.547	0.423	0.501
MK	0.705	0.091	0.785	0.035	0.869	0.015	0.475	0.465	0.788	0.055	0.681	0.155	0.841	0.014
EMK	0.798	0.089	0.812	0.075	0.869	0.055	0.530	0.616	0.799	0.138	0.814	0.117	0.870	0.029
ENK	0.500	0.603	0.481	0.638	0.423	0.784	0.465	0.723	0.628	0.435	0.585	0.515	0.521	0.562
ENM	0.811	0.076	0.812	0.075	0.886	0.040	0.500	0.666	0.832	0.094	0.809	0.124	0.870	0.029
ENMK	0.817	0.170	0.812	0.179	0.914	0.072	0.558	0.770	0.861	0.166	0.825	0.240	0.870	0.084

Parameters $X_1X_2X_3X_4$	$Y_1(2\text{-Cl})$		$Y_2(2\text{-Cl})$		$Y_3(2\text{-Cl})$		$Y_4(2\text{-Cl})$		$Y_1(2\text{-Br})$		$Y_3(2\text{-Br})$		$Y_1(3\text{-OH})$	
	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P
E	0.762	0.134	0.259	0.501	0.041	0.924	0.739	0.058	0.513	0.157	0.164	0.651	0.329	0.471
N	0.854	0.065	0.367	0.311	0.105	0.804	0.607	0.148	0.380	0.313	0.063	0.862	0.397	0.378
M	0.533	0.355	0.309	0.418	0.371	0.365	0.056	0.905	0.864	0.003	0.455	0.187	0.654	0.111
K	0.906	0.034	0.365	0.334	0.209	0.619	0.664	0.104	0.341	0.369	0.130	0.719	0.400	0.374
EK	0.936	0.123	0.398	0.596	0.399	0.649	0.739	0.206	0.591	0.276	0.167	0.906	0.400	0.706
EN	0.861	0.258	0.410	0.575	0.242	0.860	0.747	0.196	0.555	0.331	0.281	0.796	0.397	0.710
EM	0.774	0.401	0.489	0.440	0.371	0.690	0.861	0.067	0.868	0.015	0.565	0.260	0.781	0.153
NM	0.954	0.089	0.589	0.279	0.417	0.620	0.700	0.260	0.866	0.016	0.529	0.317	0.824	0.103
NK	0.966	0.067	0.367	0.648	0.811	0.069	0.809	0.120	0.521	0.386	0.647	0.150	0.400	0.706
MK	0.960	0.079	0.564	0.316	0.454	0.562	0.734	0.212	0.865	0.016	0.550	0.283	0.792	0.139
EMK	0.972	0.294	0.572	0.541	0.557	0.648	0.862	0.204	0.893	0.035	0.566	0.476	0.799	0.326
ENK	0.980	0.251	0.411	0.799	0.814	0.188	0.950	0.051	0.659	0.377	0.569	0.209	0.400	0.897
ENM	0.964	0.333	0.611	0.467	0.487	0.752	0.862	0.202	0.904	0.027	0.711	0.472	0.824	0.276
ENMK	1.000	0.000	0.680	0.556	0.823	0.369	0.950	0.186	0.930	0.050	0.735	0.338	0.986	0.055

Table 9

Calculated regressions coefficients for 2-carboxy; 4-carboxy; 3-nitro; 3-methyl; 2,5-dimethyl and 4-chlorophenylazouracil compounds

Parameters	Y ₁ (2-COOH)		Y ₃ (2-COOH)		Y ₁ (4-COOH)		Y ₃ (4-COOH)		Y ₁ (3-NO ₂)		Y ₂ (3-NO ₂)		Y ₃ (3-NO ₂)	
	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P
X ₁ X ₂ X ₃ X ₄														
E	0.116	0.784	0.162	0.702	0.114	0.789	0.638	0.064	0.844	0.156	0.180	0.700	0.135	0.749
N	0.002	0.996	0.470	0.240	0.121	0.776	0.602	0.087	0.644	0.356	0.099	0.832	0.317	0.445
M	0.385	0.346	0.549	0.159	0.750	0.032	0.087	0.824	0.211	0.789	0.532	0.219	0.289	0.488
K	0.020	0.962	0.474	0.235	0.151	0.721	0.622	0.074	0.667	0.333	0.148	0.751	0.314	0.449
EK	0.200	0.903	0.694	0.193	0.155	0.941	0.655	0.186	0.846	0.533	0.182	0.935	0.393	0.657
EN	0.256	0.844	0.727	0.153	0.122	0.964	0.645	0.199	0.866	0.501	0.237	0.891	0.411	0.629
EM	0.385	0.669	0.549	0.408	0.833	0.052	0.647	0.194	0.980	0.199	0.820	0.107	0.352	0.719
NM	0.408	0.634	0.630	0.282	0.842	0.045	0.622	0.231	0.970	0.241	0.655	0.327	0.502	0.484
NK	0.206	0.897	0.474	0.529	0.307	0.781	0.640	0.206	0.674	0.739	0.456	0.627	0.317	0.768
MK	0.395	0.655	0.646	0.259	0.833	0.052	0.634	0.214	0.925	0.380	0.653	0.329	0.484	0.513
EMK	0.418	0.837	0.872	0.098	0.839	0.148	0.669	0.358	1.0	0.000	0.919	0.099	0.533	0.686
ENK	0.377	0.877	0.730	0.338	0.319	0.924	0.696	0.307	1.0	0.000	0.564	0.727	0.417	0.838
ENM	0.472	0.772	0.852	0.127	0.844	0.139	0.661	0.373	1.0	0.000	0.910	0.115	0.575	0.619
ENMK	0.758	0.516	0.876	0.240	0.867	0.263	0.696	0.523	--	--	0.921	0.279	0.652	0.714
Parameters	Y ₁ (3-CH ₃)		Y ₃ (3-CH ₃)		Y ₁ (2,5-diCH ₃)		Y ₃ (2,5-diCH ₃)		Y ₁ (4-Cl)		Y ₃ (4-Cl)		Y ₄ (4-Cl)	
X ₁ X ₂ X ₃ X ₄	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P	MCC	P
E	0.076	0.858	0.299	0.401	0.550	0.158	0.313	0.378	0.164	0.673	0.431	0.247	0.801	0.017
N	0.198	0.639	0.212	0.557	0.518	0.188	0.264	0.461	0.280	0.466	0.320	0.402	0.714	0.047
M	0.691	0.058	0.524	0.120	0.566	0.144	0.582	0.077	0.653	0.056	0.074	0.851	0.452	0.261
K	0.241	0.566	0.247	0.491	0.515	0.192	0.296	0.407	0.287	0.453	0.401	0.285	0.727	0.041
EK	0.429	0.602	0.302	0.716	0.554	0.400	0.315	0.693	0.359	0.660	0.432	0.539	0.824	0.058
EN	0.342	0.733	0.325	0.676	0.553	0.401	0.315	0.693	0.356	0.666	0.464	0.483	0.832	0.053
EM	0.756	0.120	0.728	0.071	0.888	0.021	0.799	0.030	0.764	0.072	0.485	0.447	0.819	0.062
NM	0.826	0.057	0.700	0.095	0.867	0.031	0.794	0.029	0.842	0.025	0.386	0.617	0.733	0.145
NK	0.426	0.606	0.407	0.530	0.518	0.458	0.409	0.527	0.293	0.764	0.794	0.050	0.732	0.147
MK	0.823	0.059	0.698	0.096	0.832	0.052	0.791	0.032	0.819	0.036	0.457	0.495	0.756	0.120
EMK	0.855	0.123	0.729	0.181	0.888	0.078	0.805	0.082	0.824	0.104	0.488	0.686	0.841	0.144
ENK	0.494	0.742	0.492	0.618	0.554	0.653	0.454	0.684	0.360	0.859	0.865	0.058	0.832	0.158
ENM	0.868	0.104	0.729	0.181	0.894	0.070	0.808	0.079	0.863	0.060	0.499	0.668	0.866	0.107
ENMK	0.870	0.257	0.729	0.349	0.967	0.024	0.812	0.179	0.951	0.026	0.897	0.100	0.904	0.174

hydrogen bonding has a neglectable role when combined with dielectric constant alone or with refractive index, while has a role when combined with refractive index only (M). The combinations without E is more effective than that with E. (3) The compounds gave visible band (Y_4) e.g. 2- & 4-Cl, 2-CH₃ and 2-OCH₃ compounds were affected strongly by the three parameters (E, K & N) separated or combined with each other. However, the M parameter alone gives poor correlation but if it is combined with the other parameters, the correlation becomes good. So, the solute-solvent hydrogen bonding, refractive index and dielectric constant can explain the spectral shifts.

However, the data based on the three parameters equation give more explanation (give moderate to strong fit to the observed spectral shifts). (1) The dielectric constant or the refractive index when combined with solute-solvent hydrogen bonding and the solute permanent dipole-solvent induced dipole interaction, gave the same effects which are higher than the effects resulted from the combination of dielectric constant with solute-solvent hydrogen bonding and solute permanent dipole-solvent permanent dipole interaction. (2) The compounds which gave Y_4 (visible band) are the mostly affected by the solvent parameters based on one, two and three parameter equations. The four-parameters equation gives a best fit to the observed spectral shifts. The four combination is the more effective in the most compounds except for the compounds which gave Y_4 . However, for the 3-NO₂ compound based on Y_1 , the distribution of the solvent around the solute from the Frank-Condon principle points that the forces present are distributed in a manner to cancel each other. This explains the inapplicability of four parameters equation for the 3-NO₂. Also, the electron donor compounds are more effective than the electron withdrawing compounds by the four solvent parameters together based on $\pi-\pi^*$ transition (Y_1) and the visible bands (Y_4) and it reversed based on $n-\pi^*$ transition band (Y_2).

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