A Study of Tautomerism in Diazonium Coupling Products of 4-Hydroxycoumarin

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The spectra (^{1}H nmr, ir and uv) of a series of 3-arylazo-4-hydroxycoumarins **1a-m** indicate that such compounds exist predominantly in the keto hydrazone form **1A** both in solid state and in solution. The acid dissociation constants of the series studied were determined spectrophotometrically in 80 vol% ethanol-water mixture at 27° and ionic strength of 0.1. The results of the correlations of these constants by Hammett and Yukawa-Tsuno equations exclude the presence of the hydroxyazo form **1B** in equilibrium with **1A** in agreement with the spectral data. Also, the HMO method has been used to study tautomerism in such compounds. The results are also in full agreement with both the spectral and linear free energy correlations, the hydrazone form **1A** being the most stable. It is further shown that both the intermolecular and intramolecular hydrogen bonding favor the hydrazone tautomer.

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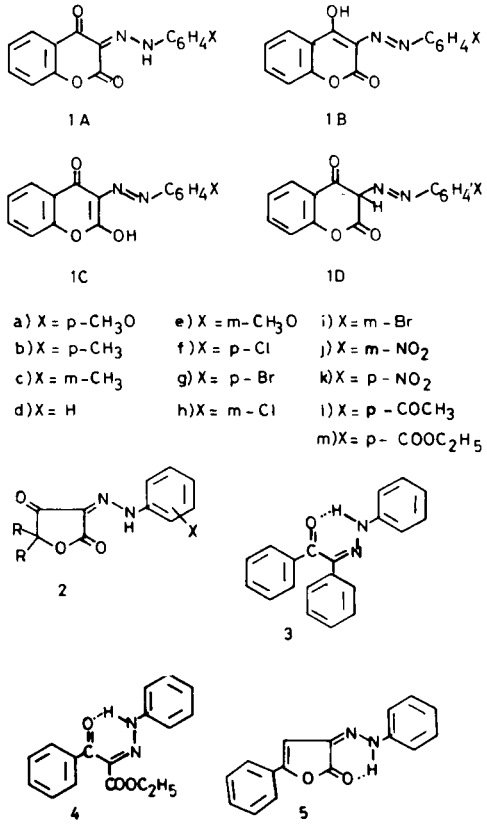
Literature cites contradicting reports regarding the tautomeric structure of the diazonium coupling products of 4-hydroxycoumarin for which four possible forms **1A-D** can be written (Scheme 1). Thus, whereas the ketohydrazone form **1A** was assigned by Huebner *et al.* [3] and Yoder *et al.* [4], others [5], from the results of a polarographic study, were in favour of the azohydroxy structure **1B**. As these compounds are structurally related to the diazonium coupling products of tetronic acid **2**, which have been shown to have the ketohydrazone form [6] (Scheme 1), it was felt necessary to reexamine the tautomeric structure of the compounds in question. For this purpose, we have prepared a series of thirteen ring substituted 3-phenylazo-4-hydroxycoumarins **1a-m** and investigated their spectra. Also, we have measured the acid dissociation constants of such a series and examined their correlations with Hammett and Yukawa-Tsuno equations. In order to obtain further insight into the tautomeric structure of such compounds, the relative stabilities of the tautomeric forms of **1d** and the effects of hydrogen bonding and solvent interaction have been investigated by Hückel molecular orbital (HMO) method. The use of spectra [3,7-10], linear free energy correlations [11-15] and HMO method [6,9,16,17] in solving the tautomeric problems in the diazonium coupling products of active methylene compounds is well established.

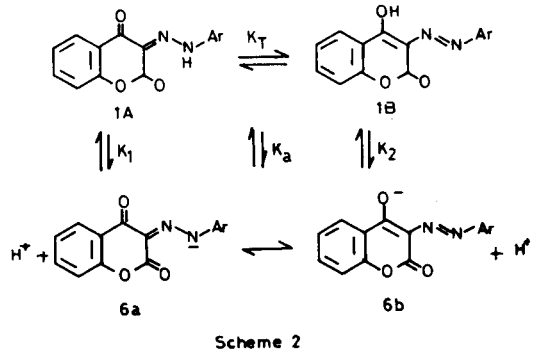


Scheme 1

Results and Discussion.

Spectroscopic Investigation.

The infrared spectral data of the compounds studied **1a-m** (Table 1) indicate that they exist in the keto hydraz-



Scheme 2

Table 1

Characteristic Spectral Data of the Studied Compounds

Compound No.	ν (KBr), cm^{-1}	δ [a] (deuteriochloroform), ppm.	λ max	(log ϵ), nm
1a	3070, 1735, 1605	16.6, 14.2, 4.0	258 (4.139)	452 (4.425)
1b	3085, 1735, 1615	16.5, 14.4, 2.35	252 (4.296)	420 (4.553)
1c	3110, 1730, 1620	16.3, 14.4, 2.4	256 (4.100)	424 (4.483)
1d	3100, 1730, 1620	16.4, 14.3	256 (3.982)	424 (4.380)
1e	3100, 1735, 1615	16.4, 14.1, 4.1	256 (4.176)	424 (4.584)
1f	3150, 1730, 1625	16.2, 14.0	256 (3.982)	428 (4.346)
1g	3100, 1730, 1620	16.4, 14.3	256 (4.068)	428 (4.469)
1h	3100, 1750, 1622	16.3, 14.1	260 (4.280)	410 (4.370)
1i	3100, 1750, 1620	16.2, 14.0	254 (4.250)	414 (4.241)
1j	3120, 1730, 1620	16.2, 14.4	256 (4.21)	400 (4.340)
1k	3120, 1730, 1625	16.3, 14.3		414 (4.716)
1ℓ	3100, 1730, 1665, 1620	16.0, 14.0, 2.8	250 (4.11)	400 (4.387)
1m	3100, 1740, 1705, 1602	16.3, 14.2, 4.4, 1.4	252 (4.120)	420 (4.355)

[a] All compounds exhibit aromatic proton multiplets in the region 7.0-8.2 ppm.

Table 2

Acid Dissociation Constants and Substituent Constants of the Studied Compounds **1a-m**

Compound No.	X	$pK_a \pm s$ [a]	σ_x	σ_x^-
1a	*p*-CH_3O	9.91	− 0.27	− 0.27
1b	*p*-CH_3	9.58	− 0.17	− 0.17
1c	*m*-CH_3	9.49	− 0.07	− 0.07
1d	H	9.15	0.00	0.00
1e	*m*-CH_3O	9.09	0.07	0.07
1f	*p*-Cl	8.32	0.23	0.23
1g	*p*-Br	8.43	0.23	0.23
1h	*m*-Cl	8.25	0.37	0.37
1i	*m*-Br	8.22	0.39	0.39
1j	*m*-NO_2	7.45	0.71	0.71
1k	*p*-NO_2	5.72	0.78	1.28
1ℓ	*p*-CH_3CO	6.90	0.50	0.84
1m	*p*-$COOC_2H_5$	7.40	0.45	0.68

[a] s = standard deviation = ± 0.02.

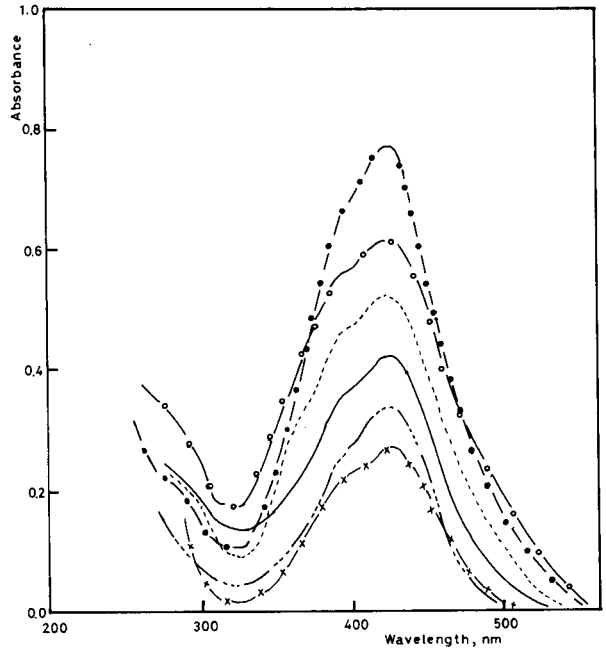


Fig. 1 Electronic absorption spectra of 3-Phenylazo-4-hydroxycoumarin in ethanol (— • —), dioxan (——), diethylether (— o —), cyclohexane (.....), acetic acid(— · —) and pyridine (— x —).

one **1A** rather than hydroxyazo form **1B**. Thus, all compounds exhibit a weak and broad NH stretching band in the region 3285-3150 cm^{-1}. The low frequency and the broadening of this band suggest that this group is strongly involved in hydrogen bonding in the solid state [18-20].

In the carbonyl region each of the compounds studied exhibits two bands near 1620 and 1720 cm^{-1} due to the stretching vibrations of the 4-carbonyl and α-pyrone groups respectively. Such an assignment is substantiated by the infrared spectra of benzil monophenylhydrazone **3** and ethyl 3-phenyl-2,3-dioxopropionate-2-phenylhydrazone **4** which show their benzoyl carbonyl stretching bands at 1630 and 1625 cm^{-1} respectively. The observed downward shift of the 4-CO stretching band in the compounds **1a-m**, by analogy to **3** and **4**, is due to the strong chelation effects [18-20] and conjugation with the C=N double bond as required by the hydrazone structure **1A**. The fact that the compounds **1a-m** show evidence for intramolecular hydrogen bonding excludes further the CH-azo form **1D** which would not possess this property due to the absence of the hydrogen NH group.

The electronic absorption spectra of the compounds **1a-m** in ethanol (Table 1) reveal, in each case, two bands in the regions 225-300 and 350-450 nm. Furthermore, the spectra of the unsubstituted derivative **1d** in different solvents were found to exhibit little, if there is any, solvent

dependence (Fig. 1). These results seem to be compatible with the hydrazone rather than the azo form, as they are similar to that of ethyl 3-phenyl-2,3-dioxopropionate 2-phenylhydrazone **4** and γ-phenyl-$\triangle^{\beta,\gamma}$-butenolide-α-phenylhydrazones **5** [21] in the same solvents. The small shifts in λ max of **1d** in different solvents is due to solute-solvent interactions. In agreement with this conclusion is the observation that the spectra of arylhydrazones derived from the reaction of quinones with *N*-alkylhydrazines, unlike those of *ortho*- and *para*-hydroxyazo compounds, are largely independent of the solvent polarity [22].

The PMR spectra of the studied compounds **1a-m** (Table 1) provide additional evidence that they have the structure of 2,3,4-chromantrione 3-arylhydrazone **1A** rather than the azo structures **1B-1D** (Scheme 1). For example, the pmr spectrum of **1d** in deuterated chloroform exhibits two broad signals near 14.4 and 16.4 ppm with integrated ratio of 1:5. Other compounds in series **1** show similar patterns. These signals undoubtedly correspond to the hydrazone NH proton resonance. The lower field signal can probably be assigned to the NH proton of the intramolecularly hydrogen bonded Z-form and the other is due to the NH proton in the *E*-form. This conclusion is substantiated by the observation that this low field pattern does not change with the solvent. For example the pmr spectra of **1d** in chloroform, dioxane and benzene showed the same pattern. Further evidence for this assignment is provided by the observation that the pmr spectrum of the ^{15}N-phenylhydrazone derivative 2,3,4-chromantrione was reported [7] to show two doublets centered at 14.2 and 16.4 ppm with J = 95 Hz. This finding indicates that the proton is attached to ^{15}N and not to the oxygen atom as in **1B** or **1C**. The OH proton resonance signal of **1B** form is expected to be in the region 9-10 ppm. It was reported that the hydroxyazo OH proton resonance comes 3-5 ppm higher than the hydrazone NH proton resonance [4]. Also, the pmr spectrum of ethyl 3-phenyl-2,3-dioxopropionate 2-phenylhydrazone **4** which is the open chain analog of **1d**, reveals its hydrazone NH near δ 13.0 ppm. The foregoing spectral data, when taken collectively, indicate that the studied compounds **1a-m** have the hydrazone structure **1A** rather than the azo tautomeric forms **1B-D** in solid (ir) and in solution (uv and pmr).

Substituent Effects on Acid Dissociation Constants.

The acid dissociation constants for **1a-m** were determined by a spectrophotometric titration method at 27.0 ± 0.1° in 80 vol% ethanol-water mixture. In all determinations the ionic strength was kept constant at 0.1. The absorption pattern was, in each case, characterized by the presence of two intense maxima near 425 (band-A) and 370 (band-B) nm. As the *p*H value increases the height of the former band decreases and simultaneously that of the latter band increases. In all cases, the decrease in band A and the increase in band B follow dissociation curves and the spectra show, in each case, one isobestic point indicating the presence of at least two species in equilibrium. Typical absorbance-*p*H curves are shown in Figure 2.

From the *p*H absorbance data at λ max of band-A, the acid dissociation constants of the compounds studied were calculated by the method of least squares using the relation:

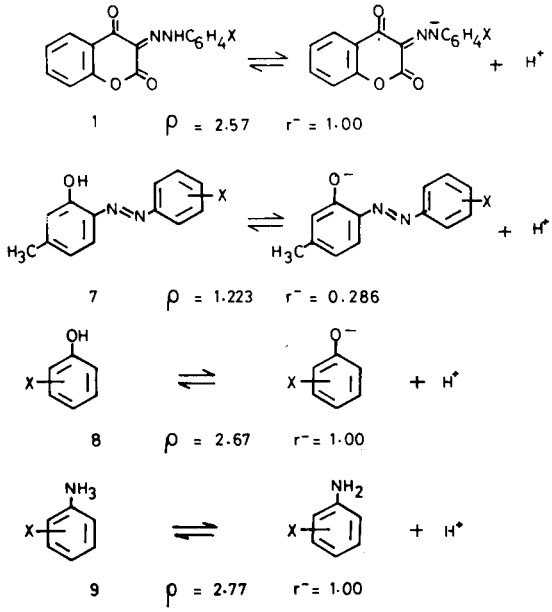
$$pH = pK_a + \log (A_i - A_b)/(A_a - A_i)$$

Table 3

Bonding Energies, BE (β units), obtained for the free, solvent H-bonded and Intramolecular H-bonded Tautomeric Forms of **1**

Form	BE, β	E(N - V_1) [a], β
	No H-Bond	
1A	24.972	0.906
1B	24.544	0.960
1C	24.521	1.045
	Solvent H-Bond	
1A	25.146	0.878
1B	24.593	0.939
1C	24.573	1.009
	Intramolecular H-Bond	
1A(*Z*)	25.497	0.905
1A(*E*)	25.438	0.923
1B	24.972	0.939
1C	24.950	1.015

[a] Energy of the first electronic transition in β units.



Scheme 3

where A_i is the absorbance of the test solution at pH_i an A_a and A_b are the absorbance values of the molecular species (*i.e.* in strongly acid medium) and the ionized species (*i.e.* in strongly alkaline medium) respectively. The values of pK_a of the compounds studied are listed in Table 2.

If the prototropic tautomerism (Scheme 2) is taken into account, the effective ionization constant K_a and the tautomeric equilibrium constant K_T are related to the dissociation constants K_1 and K_2 of the keto hydrazone and hydroxyazo forms **1A** and **1B** respectively by the equations:

$$K_a = (K_1K_2)/(K_1 + K_2) \text{ and } K_T = K_1/K_2$$

From these equations, it could be shown that

$$K_a = K_a/(1 + K_T)$$

and

$$K_a = K_2K_T/(1 + K_T)$$

According to these equations, it is obvious that a linear relation between pK_a and Hammett substituent constant σ_X would be observed only if $K_T \gg 1$ or $K_T \ll 1$, that is, when only one tautomeric form exists. However, if the two tautomeric forms **1A** and **1B** coexist in equilibrium, it would be expected to observe a nonlinear relationship, when pK_a values were plotted versus σ_X.

Another possibility is that a linear correlation between pK_a values and σ_X would be observed when $K_1 = K_2$, *i.e.* when $K_T = 1$. This possibility is excluded, however. The reason for this is obvious since the ionization of the NH and OH groups of the **1A** and **1B** forms respectively are different.

Plotting these pK_a data against σ_X values yields the graph shown in Fig. 3. It is obvious that all the substituents fall on one correlation line except the substituents with -R effect, namely, the *p*-CH_3CO, *p*-$COOC_2H_5$, and *p*-NO_2 substituents, which are capable of direct interaction with the negatively charged reaction site in **6a**. However, when the pK_a data were plotted versus σ_X^- constants, a better correlation was obtained (Fig. 4). The equation of such a correlation is:

$$pK_a = 9.177 - 2.655\ \sigma_X;\ r = 0.988;\ s = \pm 0.11$$

Table 4

Compound No.	Mp °C (Lit Mp°C)	Molecular Formula	Analysis % Calcd. (Found) C	H	N
1a	185	$C_{16}H_{12}N_2O_4$	64.86	4.08	9.45
			(64.97)	(3.97)	(9.72)
1b	190	$C_{16}H_{12}N_2O_3$	68.56	4.31	9.99
	(188-190) [3]		(68.74)	(4.25)	(9.84)
1c	168-169	$C_{16}H_{12}N_2O_3$	68.56	4.31	9.99
			(68.28)	(4.29)	(9.79)
1d	177	$C_{15}H_{10}N_2O_3$	67.66	3.78	10.52
	(178) [3]		(67.82)	(3.67)	(10.25)
1e	162-163	$C_{16}H_{12}N_2O_4$	64.86	4.08	9.45
			(64.86)	(3.99)	(9.59)
1f	232	$C_{15}H_9ClN_2O_3$	59.91	3.02	9.31
	(236) [5]		(59.91)	(2.84)	(9.49)
1g	223-225	$C_{15}H_9BrN_2O_3$	52.19	2.63	8.11
			(52.07)	(2.37)	(8.42)
1h	216-217	$C_{15}H_9ClN_2O_3$	59.91	3.02	9.31
			(59.95)	(2.89)	(9.46)
1i	230-232	$C_{15}H_9BrN_2O_3$	52.19	2.63	8.11
			(52.24)	(2.52)	(8.29)
1j	214-215	$C_{15}H_9N_3O_5$	57.88	2.91	13.50
			(57.71)	(2.90)	(13.51)
1k	264-265	$C_{15}H_9N_3O_5$	57.88	2.91	13.50
	(265) [31,32]		(58.03)	(2.75)	(13.48)
1ℓ	228-230	$C_{17}H_{12}N_2O_4$	66.23	3.92	9.08
			(66.36)	(3.72)	(9.05)
1m	188-189	$C_{18}H_{14}N_2O_5$	63.90	4.17	8.28
			(63.79)	(3.99)	(8.29)

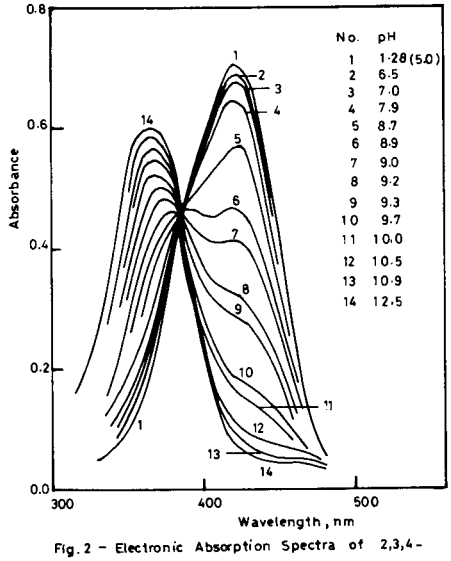


Fig. 2 – Electronic Absorption Spectra of 2,3,4-Chromantrione-3-phenylhydrazone at various pH in 80%(v/v) Ethanol-Water.

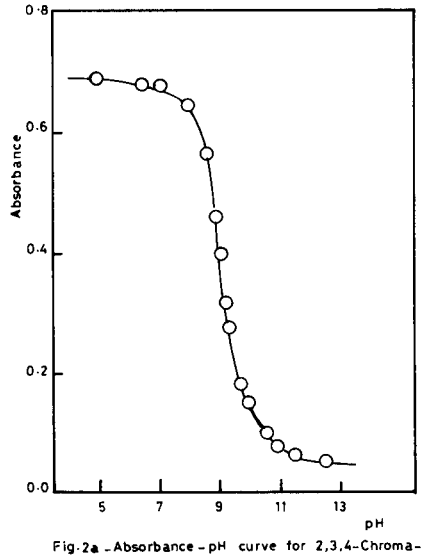


Fig. 2a – Absorbance-pH curve for 2,3,4-Chromantrione-3-phenylhydrazone at λ 420 nm.

This excellent correlation indicates that the parameter r^- in the Yukawa-Tsuno equation: $pK = pK_o + \varrho[\sigma_X + r^-(\sigma_X^- - \sigma_X)]$ [23], and which gives the contribution of the resonance effect of the substituent varied, is close to unity for the series studied.

Following the foregoing argument, the linearity observed between pK_a values and σ_X^- constants can be taken as an evidence that the diazonium coupling products **1a-m** under study exist in one tautomeric form. In addition, comparison of the values of ϱ (2.655) and r^- (1.0) obtained for the studied compounds with those reported for the ionization of *o*-arylazophenols **7** [24], phenols **8** [24,25] and anilinium ions **9** [26] in 50% ethanol-water (Scheme 3), suggests that the predominant form of the compounds in question, is the keto hydrazone structure **1A**. This is because, if the azohydroxy form **1B** were predominant, the values of ϱ and r^- would be expected to be close to those of series **7** where the substituent effects are transmitted across the azo link to the reaction site. However, the values obtained for ϱ and r^- of the studied compounds, being close to those of **8** and **9**, doubtless indicate the similarity between the three series (**1**, **8** and **9**) where the substituent is in direct interaction with the reaction site.

HMO Consideration.

The values of bonding energies, BE, of the three tautomeric forms **1A-1C** for the coupling products of 4-hydroxycoumarin are given in Table 3. These data indicate that the order of stability of such tautomeric structures is **1A** (Hydrazone) > **1B** (Azo-4-OH) > **1C** (Azo-2-OH). The

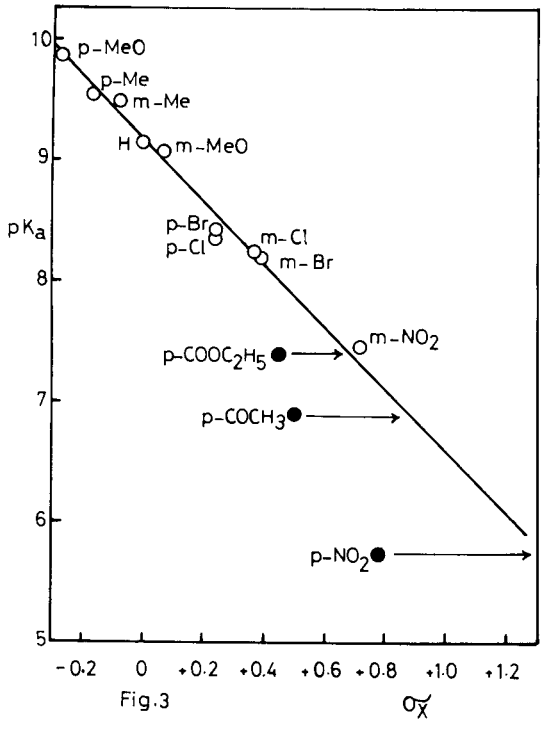
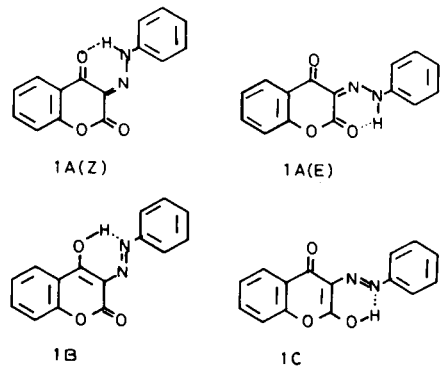


Fig.3



Scheme 4

form **1D** is expected to be least stable because of interrupted conjugation between the arylazo group and the heterocyclic portion of the molecule. The results appear to be in agreement with the experimental data outlined in the previous section.

The bonding energy for the resonance stabilized anion **6** was also calculated and found to be 23.991 β. The difference between this value and the bonding energies of the tautomers **1A-C** are as follows: $\triangle BE(\mathbf{1A\text{-}6}) = 0.981\ \beta$, $\triangle BE(\mathbf{1B\text{-}6}) = 0.553\ \beta$ and $\triangle BE(\mathbf{1C\text{-}6}) = 0.530\ \beta$. These values indicate that the acidity of these three tautomers decreases in the order **1C** > **1B** > **1A**. Because in acid-base equilibria of various tautomers, the tautomer with higher acidity is considered to be less stable [27], it is not unreasonable to conclude that the azo-2-OH tautomer **1C** is the least stable and that the ketohydrazone tautomer **1A** is the most stable among the three tautomers **1A-1C**.

Table 5

HMO Heteroatom Parameters Used to Study the Azo-Hydrazone Tautomerism of Diazonium Coupling Products of 4-Hydroxycoumarin

$\alpha_X = \alpha + h_X\beta$ $\quad b_{XY} = k_{XY}\beta$

Azo	Hydrazone	Anion
$h_N = 0.5$	$h_{NH} = 1.5$	$h_N = 1.75$ [a]
$h_O = 2.0$	$h_N = 1.0$	$h_N = 0.5$ [b]
$k_{CN} = 0.9$	$k_{C\text{-}NH} = 0.7$	$h_{C(N)} = 0.25$
$k_{NN} = 1.0$	$k_{C=N} = 1.1$	$h_O = 1.25$
$k_{CO} = 0.8$	$K_{HN} = 0.7$	$k_{C\backsim N} = 0.8$
	$C_{C=O} = 1.0$	$k_{N\backsim N} = 0.7$
		$k_{C\backsim O} = 0.9$

Hydrogen bonding to the solvent molecule (SH = solvent):

$\alpha_{XH\ldots SH} = \alpha_X - 0.2\beta$ $\quad \alpha_{Y\ldots HS} = \alpha_Y + 0.2\beta$

Intramolecular hydrogen bonding:

$\alpha_{XH} = \alpha_X - 0.2\beta$ $\quad \alpha_{Y\ldots H} = \alpha_Y + 0.2\beta$

$\beta_{X(H)Y} = 0.2\beta$

[a] N adjacent to the aryl group. [b] N adjacent to the coumarin group.

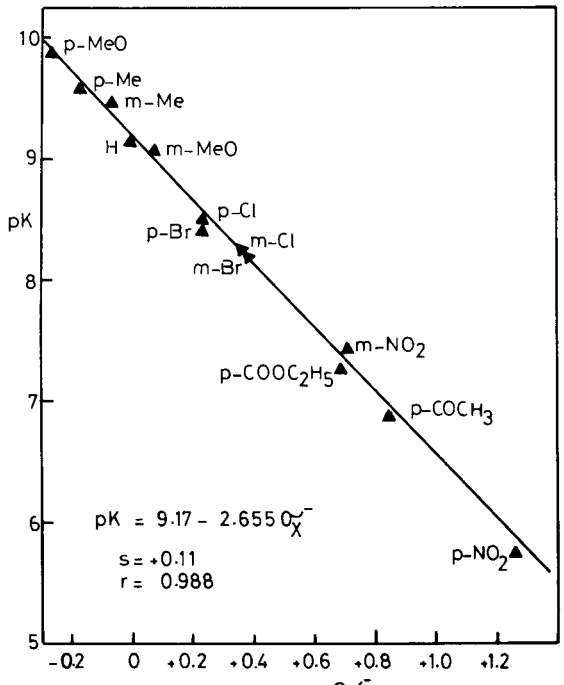


Fig. 4

Because tautomeric equilibria are solvent dependent it was thought to examine the effect of interaction with a protic solvent *via* hydrogen bonding upon the relative stability of the three major tautomers **1A-1C** (Scheme 1). For this purpose, the approach used to correlate solvent effects in the electron spin resonance spectra of semiquinone radicals has been adopted [28,29]. The effect of intermolecular hydrogen bonding with a protic solvent upon the stabilities of the three tautomeric forms **1A-1C** are given in Table 3. In addition to the bonding energies, the energies of the N - V_1 transition, E(N - V_1), are given. The results indicate that intermolecular hydrogen bonding with solvents increases the stability of all tautomeric forms. The stabilization is most pronounced in the case of the ketohydrazone form **1A**. Also, it seems worth mentioning that solvent interactions, as expected, decrease the energy of the N - V_1 transition for all tautomeric forms.

To cast some light on the configuration of the most stable form **1A**, the effect of intramolecular hydrogen bonding upon its stability has been examined and compared with **1B** and **1C** (Scheme 4). The treatment developed by Pullman and Pullman [30] for intramolecular hydrogen bonding was used in this study. The results are summarized in Table 4. The data indicate that intramolecular hydrogen bonding increases the stability of both forms **1A**(*Z*) and **1A**(*E*) and the forms **1B** and **1C** as well. The stabilization of the **1A**(*Z*) is more than **1A**(*E*). Furthermore, both forms **1A**(*Z*) and **1A**(*E*) are more stable than the chelated azo forms **1B** and **1C**.

In conclusion, the results of this theoretical treatment, while they are in complete agreement with the experimental data outlined in the previous sections, they clearly indicate that the diazonium coupling products of 4-hydroxycoumarin have the hydrazone structure of 2,3,4-chromantrione-3-arylhydrazone **1A**. They indicate that this structure is the most stable form and it remains so in different situations.

EXPERIMENTAL

Melting points were measured on Bockmonoscop unit and are uncorrected. The infrared spectra of the compounds in potassium bromide were obtained using Zeiss Infrarot-spectrophotometer model IMT16. The ultraviolet spectra were measured on a Pye-Unicam SP8000 ultraviolet spectrophotometer. The proton magnetic resonance spectra were obtained in deuterated chloroform with a Varian EM-390-90 MHz spectrometer. Microanalyses were performed on Perkin Elmer elemental analyzer, model 240-B at the microanalytical laboratory of King Abdulaziz University.

Preparation of 2,3,4-Chromantrione 3-Arylhydrazones, **1a-m**. General Method.

4-Hydroxycoumarin (8.2 g, 0.05 mole) was dissolved in a solution of anhydrous sodium carbonate (16 g, 0.015 mole) in water (250 ml). The resulting solution was cooled in an ice-salt bath to 0° and was treated with a cold (0-5°) solution of the appropriate diazonium salt prepared by diazotizing the corresponding arylamine (0.05 mole) in 36 ml of hydrochloric acid (6 *M*) with sodium nitrate (4.2 g, 0.06 mole) in water (50 ml). The addition of the diazonium salt solution took 30 minutes while stirring the reaction mixture. After the addition was completed, the mixture was stirred for further 30 minutes and left overnight in the ice-chest. The precipitated colored solid was collected and washed thoroughly with water. Purification was usually effected by crystallization from acetic acid. The compounds prepared together with their physical constants are listed in Table 4.

Determination of pK_a.

The acid dissociation constants of the compounds **1a-m** were determined spectrophotometrically in 80 vol% ethanol-water mixture at 27° ± 0.1° and an ionic strength 0.1. A Unica Pye-Unicam digital *p*H meter pW 9409 fitted with a combined glass electrode type 518635 was employed for the measurement of *p*H. The instrument was accurate to ± 0.01 *p*H unit. It was calibrated using two standard Beckman buffer solutions of *p*H 4.01 and 7.00. The *p*H meter readings (B) recorded in ethanol-water solutions were converted to hydrogen ion concentration [H^+] by means of the widely used relation of van Uitert and Haas [33] namely:

$$-\log [H^+] = B + \log U_H$$

where log U_H is the correction factor for the solvent composition and ionic strength used for which B is read. For this purpose, readings were made on a series of solutions containing known amounts of hydrochloric acid and sodium chloride such that the ionic strength was equal to 0.1 in 80% ethanol-water at 27°. The value of log U_H was found to be -0.55.

The experimental procedure followed in the determination of the pK_a constants and their calculations from the absorbance-*p*H data have already been described [14]. The pK_a values obtained were reproducible to within 0.02 pK_a unit. The results are summarized in Table 2.

HMO Calculations.

The HMO calculations were carried out in the usual way using an IBM 360/65 computer. The values of the empirical parameters adopted in this work (Table 5) are based on those given by Kuder [34].

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