Electronic Spectra, Solvatochromic Behaviour, and Acidity Constants of Some New Azocoumarin Derivatives

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The UV visible electronic spectra of some azocoumarin dyes derived from 6-aminocoumarin have been studied. The different bands observed have been assigned to the proper electronic transitions. The compounds exist mainly in the azo form but some of them exhibit an azo $\rightleftharpoons$ hydrazone tautomeric equilibrium. Solvatochromic behaviour of these compounds was investigated by studying their visible spectra in pure and mixed organic solvents of different characters. The longest wavelength band displayed by the azocoumarin derivatives in DMF solution is assigned to an intermolecular CT transition. The solvated H-bonding complexes formed between DMF and 8-hydroxyquinoline derivatives were investigated. ΔG and K_f values of these complexes have been determined. The acidity constants of six compounds were determined from the spectra in aqueous-ethanolic solutions of varying pH values.

The widespread applications of the azo compounds as dyes, as acid-base, redox indicators, metallochrome and histological stains have attracted the interest of many investigators in the study of their acid-base and spectral properties [1—5]. Therefore, this paper presents an investigation of the electronic spectra of some new azocoumarin derivatives in pure and mixed organic solvents of different polarities and buffer solutions of varying pH's. Azocoumarin dyes [6] were applied for dyeing polyester fibre and showed high fastness properties such as sublimation, light, washing, perspiration, and rubbing fastness.

The electronic absorption spectral characteristics (λ_{max}, ε_{max} values) of the investigated compounds (*I—VIII*, see Scheme 1) in methanol, in the wavelength range 240—600 nm, are reported in Table 1. The data reveal that the compounds comprise two to four bands (except compound *VIII* comprising five bands) in the UV and visible regions, depending on their molecular structures. The band of the shortest wavelength appearing in the range 230—270 nm is ascribed to a π—π^* transition of the benzenoid system of the compounds. This assignment is quite reasonable since λ_{max} of this band is slightly altered on transfer from one derivative to another indicating the local nature of such a transition.

The second band observed in the UV spectra (compound *III*) in the wavelength range 305—330 nm is attributable to an n—π^* electronic transition. This assignment is supported by the disappearance of this band in acid medium where excitation of the n-electrons is expected to be hindered by protonation.

The third main visible band in the region 390—490 nm can be assigned to π—π^* transition involving the whole electronic system of the compounds with a considerable charge-transfer character originating mainly from the phenolic or naphtholic moiety and pointing towards the hetero coumarin ring which is characterized by a high electron-accepting character. The charge-transfer nature of this band is deduced from its broadness [7] as well as from the sensitivity of its λ_{max} to the type of substituent attached to the azo coupler. This band acquires an appreciable shift towards lower energy (red shift) when R is an electron donor (compounds *I, III, IV, VII*) compared to its position in the case of R being an electron acceptor (compounds *V* and *VI*). This shift can be considered as good evidence for the CT character of this band.

The visible spectrum of compounds *II* and *VIII* in methanol is different from those discussed above, the intramolecular CT band being broad and exhibiting two maxima (Fig. 1, Table 1). This behaviour can be attributed to the existence of an azo $\rightleftharpoons$ hydrazone tautomeric equilibrium originating from the OH group [2]. Accordingly, the shorter wavelength bands (for compounds *II, VIII* at 425 nm, 427 nm, respectively in methanol) correspond to an intramolecular CT within the azo form, and the longer wavelength (at 475 nm) is due to the CT transition within the hydrazone form. The low excitation energy of this transition in the case
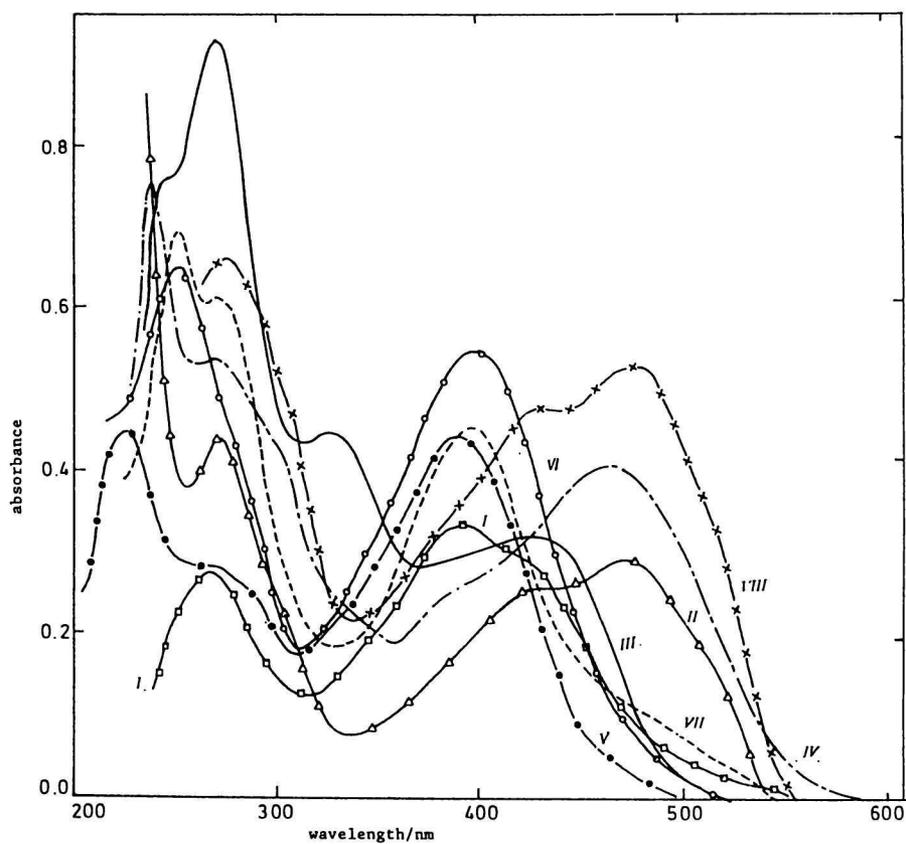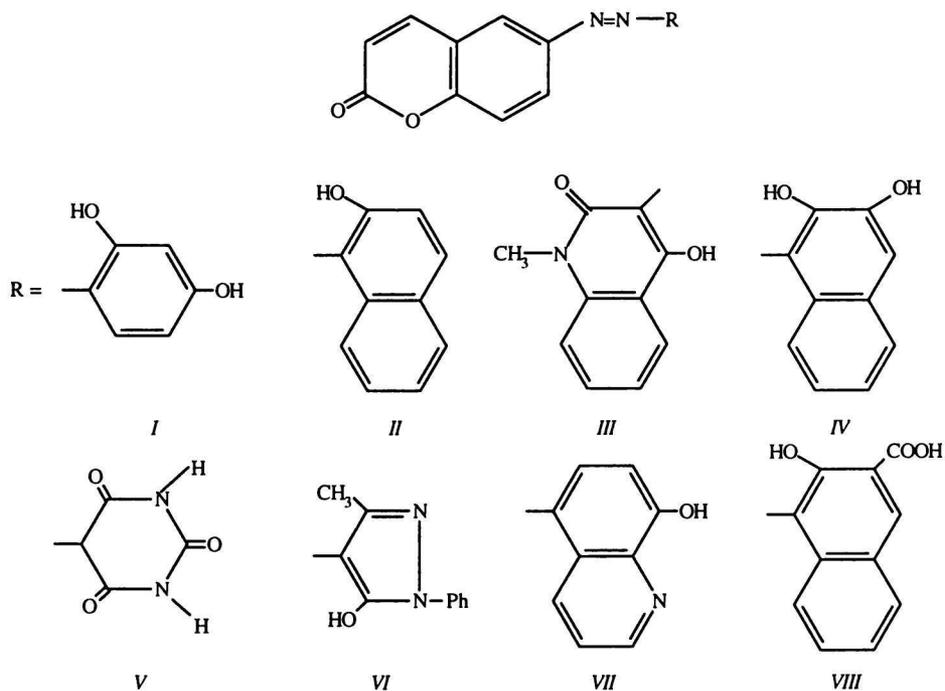
Scheme 1

Fig. 1. Electronic absorption spectra of 2—4×10^{-5} mol dm^{-3} methanolic solutions of the azocoumarin derivatives *I—VIII*. $\square$ *I*, $\triangle$ *II*, —— *III*, $-\cdot-$ *IV*, $\bullet$ *V*, $\circ$ *VI*, - - - - *VII*, $\times$ *VIII*. For *I*, *II*, *III*, *VII*, *VIII* $c = 4 \times 10^{-5}$ mol dm^{-3}, for *IV*, *VI* $c = 3 \times 10^{-5}$ mol dm^{-3}, and for *V* $c = 2 \times 10^{-5}$ mol dm^{-3}.

Table 1. Electronic Spectral Data of Some Azocoumarin Derivatives in Different Solvents at 25 °C

Compound	Methanol		Ethanol		Acetone		Acetonitrile		DMSO		DMF	
	λ/nm	$\varepsilon_{max} \cdot 10^{-3}$	λ/nm	$\varepsilon_{max} \cdot 10^{-3}$	λ/nm	$\varepsilon_{max} \cdot 10^{-3}$	λ/nm	$\varepsilon_{max} \cdot 10^{-3}$	λ/nm	$\varepsilon_{max} \cdot 10^{-3}$	λ/nm	$\varepsilon_{max} \cdot 10^{-3}$
I	270	7.3	265	13.0	–	–	265	17.3	270	20.0	270	13.3
	390	8.5	390	13.0	390	7.5	390	17.0	390	18.0	400	14.5
	430 sh	7.0	430	12.8	430 sh	7.0	425 sh	13.7	410 sh	12.8	430 sh	14.0
									510 sh	12.0	510 sh	13.0
II	–	–	230	24.0	–	–	–	–	–	–	–	–
	270	11.4	270	11.0	–	–	280	12.0	–	–	275	17.0
	425	6.3	425	6.6	425	9.4	420[a]	12.5	430	9.0	–	–
	475	7.5	475	7.5	470	9.7	475[a]	12.5	480	10.2	430 sh	7.2
	510 sh	5.6	510 sh	5.6	510 sh	6.2	510 sh	8.0	510 sh	7.2	–	–
III	245	20.0	–	–	–	–	230	–	–	–	–	–
	265	25.0	265	14.4	–	–	265	2.1	270	21.0	275	17.0
	330	11.3	336	6.3	330	5.8	325 sh	0.7	330 sh	9.4	330	10.1
	–	–	370[a]	5.0	400 sh	5.5	–	–	–	–	–	–
	430	8.3	430[a]	5.0	430	5.1	430	1.4	430	7.1	436	7.2
IV	236	25.0	–	–	–	–	245	7.3	–	–	–	–
	270	18.0	270	20.5	–	–	275	7.9	275	36.0	275	16.3
	305 sh	16.0	305 sh	15.0	316 sh	15.5	308	6.6	310 sh	9.6	310 sh	10.0
	465	14.0	465	17.5	475	18.2	480	8.4	480	38.5	480	12.3
V	230	16.5	230	16.0	–	–	235	12.7	–	–	–	–
	270	15.0	270	14.5	–	–	270	14.7	270	12.2	270	13.0
	395	20.0	394	19.5	395	10.7	395	14.0	395	14.0	395	16.0
VI	250	25.0	230	20.5	–	–	265	19.0	265	24.0	270	14.5
	395	13.8	398	24.6	400	16.8	400	12.0	405	20.0	415	12.0
	–	–	–	–	–	–	–	–	460 sh	10.0	460 sh	10.0
VII	245	14.0	245	11.4	–	–	245	18.0	–	–	–	–
	270	12.0	265	11.0	–	–	265	15.0	270	19.0	270	15.0
	395	11.5	395	9.0	390	15.0	390	14.0	405	17.6	410	12.6
	490 sh	3.0	490 sh	1.8	–	–	–	–	–	–	520	6.8
VIII	270	20.0	270	20.0	–	–	270	20.0	270	18.2	270	20.0
	305 sh	10.0	305 sh	10.0	305 sh	10.0	305 sh	5.0	305 sh	5.8	305 sh	5.0
	427	12.0	427	12.0	424	12.6	424	12.6	430	11.0	430	12.7
	475	13.3	475	13.1	470	13.0	475	13.0	480	12.0	470	13.7
	510 sh	7.5	510 sh	7.5					520 sh	6.4	510 sh	7.5

of the hydrazo species relative to the corresponding one in the azo compound is presumably due to the quinonoid structure of the former isomer which is expected to facilitate such a type of transition.

Solvent Effect on the Electronic Spectra

The electronic absorption spectra of the title dyes are studied in organic solvents of different polarities, *viz.* acetonitrile, acetone, ethanol, methanol, DMSO, and DMF. This is done with the intention of investigating the solvatochromic behaviour of these compounds. The UV bands (π—π^* and n—π^*) suffer small solvent shifts, a behaviour which is characteristic of these types of electronic transitions (*cf.* Table 1 and Fig. 1). The longer-wavelength visible band appearing in the wavelength range 390—490 nm is the most sensitive one towards the nature of the organic solvent, a behaviour that can be considered as further evidence for the CT nature of this band. Fig. 2 is a representative example for the solvatochromic behaviour of the dyes under investigation. It could be recognized that the main visible band (390—410 nm) of compound *VII* (Fig. 2) exhibits an apparent shift towards longer wavelengths on transfer according to the sequence: acetonitrile, acetone, ethanol, methanol, DMSO, DMF. This shift does not agree with the change in the polarity of the organic solvent. Therefore it can be considered to correspond to the net of several solvent effects such as polarity, basicity, and H-bond-accepting ability.

The visible spectra for compound *VII* in DMF comprise a new band appearing at longer wavelength (520 nm, Fig. 2) exceeding by far the usual solvent shift. This behaviour can be interpreted on the basis that the solute molecules are liable to form a solvated complex with DMF molecules through an intermolecular H-bonding [8]. Since charge-transfer forces
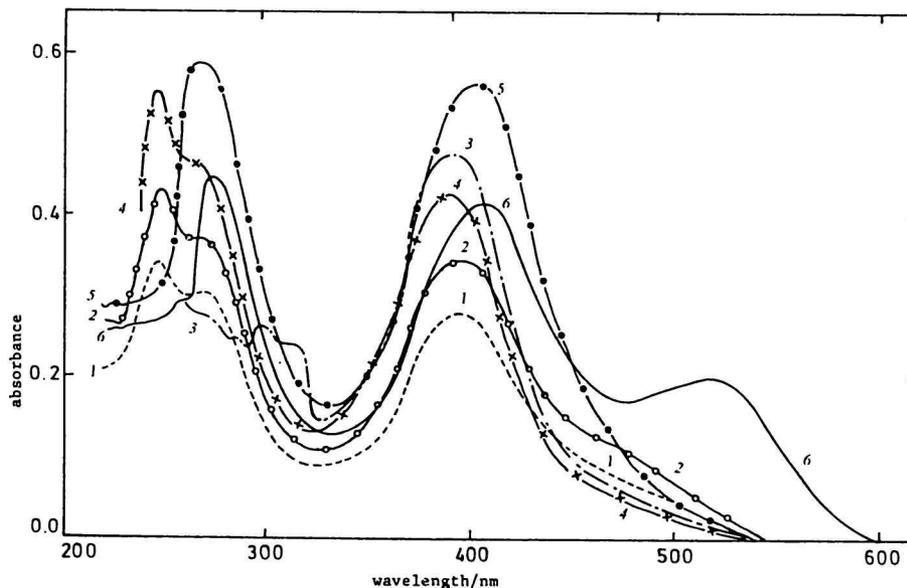
Fig. 2. Electronic absorption spectra of 3×10^{-5} mol dm^{-3} solutions of compound *VII* in organic solvents. *1.* Acetonitrile, *2.* acetone, *3.* ethanol, *4.* methanol, *5.* DMSO, *6.* DMF.

play an important role in H-bonding, this additional band is presumably due to an intermolecular CT transition [6]. This involves an electron transfer from the lone pair of electrons at the oxygen atom of the DMF molecule (ψ_{01}) to the antibonding orbital of the OH bond of the phenolic moiety. The appearance of this band in DMF as a solvent can be ascribed to its high basicity as well as its pronounced character as a strong proton acceptor. Good convincing evidence for the intermolecular CT nature of this band is attained from the nonlinear relationship between the absorbance of this band and the molar concentration of the azo compound.

Spectra in Mixed Organic Solvents

The visible spectra of compound *VII* are recorded in DMF—CCl$_4$, DMF—MeCN, DMF—CHCl$_3$, DMF —EtOH, DMF—MeOH, DMF—benzene, and DMF— (Me)$_2$CO mixtures. This is performed in order to study the solvated H-bond complexes liable to be formed between the solute molecule and DMF. Thus the spectral behaviour of compound *VII* in (Me)$_2$CO, CCl$_4$, EtOH, MeOH, benzene, MeCN, and CHCl$_3$ as solvents, each containing successively increasing amounts of DMF, was studied. It is evident that with increasing DMF concentration the absorbance of the intramolecular CT band decreases, whereas a new band appears [9] at a longer wavelength (Fig. 3). Generally, the spectra recorded in all the mixed solvents investigated exhibit an isosbestic point which indicates the establishment of an equilibrium between the free and H-bond-solvated species of the compound. This behaviour indicates that DMF molecules have a greater tendency to form solvated complexes with the

solute molecule than CCl$_4$, MeCN, (Me)$_2$CO, EtOH, MeOH, CHCl$_3$, and benzene [5]. This is due to the low ionization potential of DMF as well as to high H-bond-accepting character.

The value of molecular complex formation constant (K_f) is determined from the variation of absorbance obtained by increasing the polar solvent concentration at a given wavelength. The equation used is taken from Ref. [10].

$$\log C_{\mathrm{DMF}} = \log K_f + \log \frac{A - A_o}{A_1 - A} \qquad (1)$$

where A_o is the absorbance in a low-polarity solvent, A_1 is the absorbance in a high-polarity solvent, A is the absorbance in a mixed solvent. Gibbs energy (ΔG) values of the solvated complexes are obtained from the relation given in [8].

$$\Delta G = -RT \ln K_f \qquad (2)$$

The values of K_f and ΔG of the various molecular complexes liable to exist in solution are given in Table 2.

Acid-Dissociation Constants

The acidity constant pK_a of the carboxylic group of compound *VIII* as well as the acidity constants pK_a of the compounds *I—III*, *VI—VIII* (concerning OH group), respectively, were determined by considering the spectral behaviour of these compounds in universal buffer solution (pH = 3.5—12) containing $w =$ 16.5 % ethanol to ensure the complete solution of the compounds. The spectra recorded in universal buffer solutions for all compounds (5.0×10^{-5} mol dm^{-3})
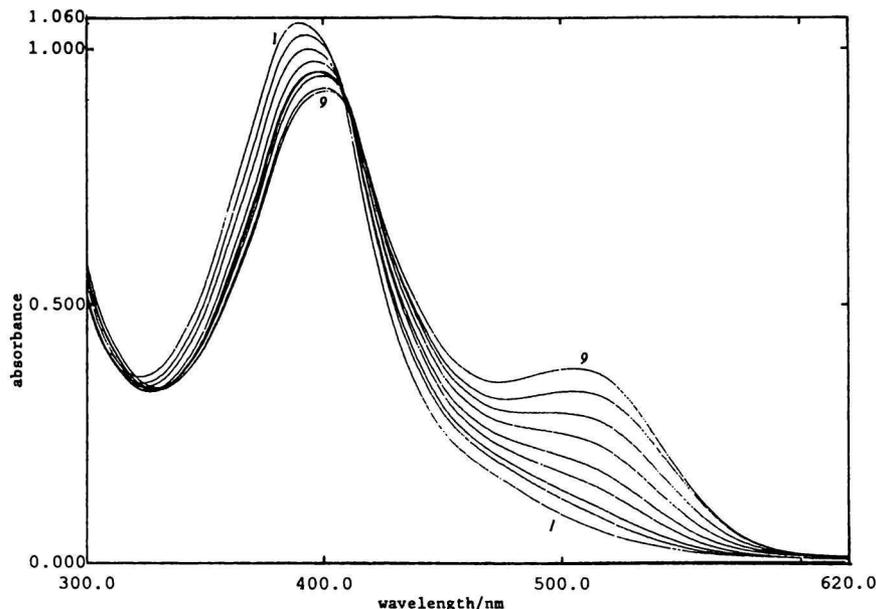
Fig. 3. Visible electronic absorption spectra of 5.0×10^{-5} mol dm^{-3} solutions of compound *VII* in DMF—CHCl$_3$ mixtures. *1.* 1.29 mol dm^{-3} DMF, *2.* 2.58 mol dm^{-3} DMF, *3.* 3.87 mol dm^{-3} DMF, *4.* 6.45 mol dm^{-3} DMF, *5.* 7.74 mol dm^{-3} DMF, *6.* 9.03 mol dm^{-3} DMF, *7.* 10.32 mol dm^{-3} DMF, *8.* 11.61 mol dm^{-3} DMF, *9.* 12.90 mol dm^{-3} DMF.

Table 2. Values of K_f and ΔG for the H-Bonding-Solvated Complexes of 8-Hydroxyquinoline Derivative (Compound *VII*)

System	log K_f	K_f	$\Delta G/(\text{kJ mol}^{-1})$
DMF—CCl$_4$	0.92	8.32	1.26
DMF—MeCN	0.96	9.12	1.32
DMF—(Me)$_2$CO	0.87	7.50	1.20
DMF—EtOH	0.93	8.51	1.28
DMF—MeOH	0.95	8.91	1.30
DMF—CHCl$_3$	0.90	7.94	1.24
DMF—Benzene	0.89	7.76	1.22

display a clear isosbestic point (*cf.* Fig. 4). This indicates the existence of an equilibrium, in such solutions for each compound, between neutral and ionic forms (HA $\rightleftharpoons$ H$^+$ + A$^-$). The absorbance—pH relations constructed at the selected wavelengths show good S-shaped curves comprising one inflection except for compound *VIII* where its absorbance—pH curves displayed two inflections [5]. This behaviour indicates the acid character of the different equilibria established in this pH range as well as the fact that the ionization of the substituent COOH group in case of the compound *VIII* occurs in a stepwise manner. The mean pK_a in COOH group is 4.5.

The pK_a values for compounds were determined making use of three different spectrophotometric methods, namely the half curve-height, isosbestic point, and the limiting absorbance [11, 12]. The mean
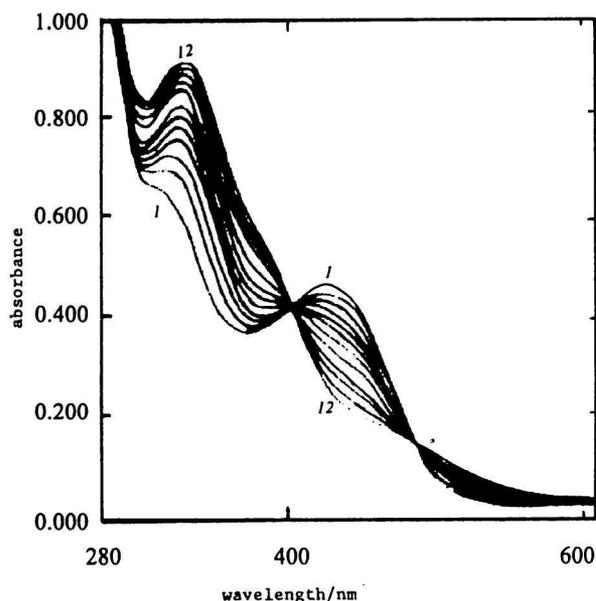

Fig. 4. Absorption spectra of compound *III* ($c = 5.0 \times 10^{-5}$ mol dm^{-3}) in universal buffer solutions containing $w = 16.5$ % ethanol. pH*: *1.* 4.25, *2.* 5.30, *3.* 6.50, *4.* 8.32, *5.* 8.94, *6.* 9.20, *7.* 9.50, *8.* 9.70, *9.* 9.95, *10.* 10.15, *11.* 10.50, *12.* 11.20.

pK_a (of OH group) values obtained are recorded in Table 3.

In the light of the determined ionization constant values of the OH in the phenolic moiety, the acidity decreases (pK_a increase) according to the following

Table 3. Physical Data of Compounds *I—VIII*

Compound	Formula M_r	w_i(calc.)/% w_i(found)/%			M.p./°C	IR $\bar{\nu}$/cm^{-1}	Mean pK_a
		C	H	N			
I	C$_{15}$H$_{10}$N$_2$O$_4$ 282.26	63.83 63.76	3.55 3.49	9.93 9.86	276	3388 (OH); 3208 (NH); 1718^a(C=O), 1614 (C=N), 1224, 1175 (C—O)	8.20
II	C$_{19}$H$_{12}$N$_2$O$_3$ 316.084	72.15 72.16	3.80 3.77	8.86 8.83	220	3309 (OH); 3126 (NH); 1720^a(C=O), 1614 (C=N), 1257, 1208, 1163 (C—O)	11.50
III	C$_{19}$H$_{13}$N$_3$O$_4$ 347.33	65.71 65.75	3.75 3.73	12.10 12.09	196	3432 (OH); 1714^a, 1684^b(2C=O); 1626 (C=N); 1466 (N=N), 1274, 1183 (C—O)	9.20
IV	C$_{19}$H$_{12}$N$_2$O$_4$ 332.32	68.67 68.62	3.61 3.58	8.43 8.41	178	3461 (OH); 3102 (NH); 1719^a (C=O); 1629 (C=N); 1261, 1199 (C—O)	
V	C$_{13}$H$_{18}$N$_4$O$_5$ 310.31	52.00 51.87	2.67 2.63	18.67 18.65	> 300	3437 (OH); 3184 (NH); 1715^a, 1666^c, 1658^d (3 C=O); 1638 (C=N); 1431 (N=N), 1255, 1138 (C—O)	
VI	C$_{19}$H$_{14}$N$_4$O$_3$ 346.35	65.90 65.85	4.05 4.02	16.18 16.16	263	3380 (OH); 1714^a (C=O); 1622 (C=N); 1458 (N=N), 1266 (C—O)	8.00
VII	C$_{18}$H$_{11}$N$_3$O$_3$ 317.30	68.14 68.11	3.47 3.46	13.25 13.21	292	3309 (OH); 1717^a (C=O); 1639 (C=N); 1431 (N=N), 1209, 1158 (C—O)	7.90
VIII	C$_{20}$H$_{12}$N$_2$O$_5$ 360.33	66.67 66.58	3.33 3.31	7.78 7.72	216	3416 (OH); 3258 (NH); 1717^a, 1702^e (2C=O); 1623 (C=N); 1243, 1202, 1162 (C—O)	11.60

a) ν(C=O) of coumarin, *b*) ν(C=O) of *tert*-amide, *c*) ν(C=O)$_{sym}$ of the barbituric acid, *d*) ν(C=O)$_{other}$ of the the barbituric acid, *e*) ν(C=O) of the carboxylic group.

azo form   hydrazone form
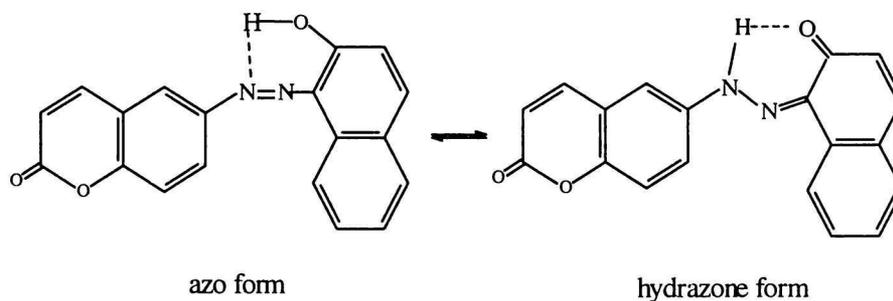
Scheme 2

sequence: *VII* < *VI* < *I* < *III* < *II* < *VIII*.

The pK_a values of the OH in compounds *II* and *VIII* are higher than those of the other compounds, this may be due to (azo-hydrazo tautomerism, Scheme 2) the possible interaction of the OH and the nitrogen atom of the azo moiety, through intramolecular H-bonding. This in turn results in a difficult liberation of the OH proton [13].

EXPERIMENTAL

The synthesized 6-aminocoumarin [14, 15] was diazotized in the usual way by dissolving it in hydrochloric acid, cooling the solution to 0—5 °C, then adding an equivalent amount of ice-cooled sodium nitrite solution with vigorous stirring. The cooled diazonium salt solution was used for coupling with the suitable coupling agent [15].

The azo compounds were washed with water and dried. The crude compounds were crystallized from aqueous ethanol ($\varphi_r = 1 : 1$) and dried *in vacuo* over silica gel. The characterization of the prepared compounds was determined by elemental analysis (Table 3). The structures of the prepared azocoumarin derivatives are presented in Scheme 1.

The organic solvents used (MeOH, EtOH, (Me)$_2$CO, MeCN, DMSO, DMF) were all of anal. grade (Merck or BDH). Solutions (10^{-3} mol dm^{-3}) of the compounds (*I—VIII*) were prepared by dissolving the accurately weighed amount of the target compound in the required amount of the appropriate solvent. Solutions of lower concentrations, used in the spectral measurements, were obtained by accurate dilutions. Universal buffer solutions were prepared as given by *Britton* [16]. Buffer solutions containing $w = 16.5$ % ethanol were used in order to overcome the low solubility of the azo compounds in pure aqueous medium. The pH values were checked using an Orion 501 ionalyzer accurate to ±0.01 pH unit. The electronic spectra were recorded on a CECIL 599 spectrophotometer

at 25 °C using 1 cm matched silica cells. Infrared spectra of the solids were recorded by a Perkin—Elmer 599B spectrophotometer using KBr discs.

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