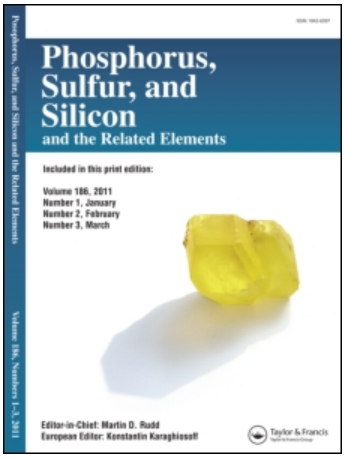

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NOVEL SULPHOARYLAZO 4-PYRAZOLONE-BASED TARTRAZINE DYE ANALOGUES

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In a multistep synthesis, a novel series of 4-pyrazolone–based tartrazine dye analogues were prepared benzimidazol -5-yl acetoacetamide derivative I. Chemical structure of the hitherto prepared dyestuffs were confirmed on the basis of correct elemental analysis as well as spectral data. The degree of exhaustion of the hitherto synthesized 3-[2-(oxoimidazo-5-yl) carboxamido] tartrazine dye analogues was determined and found to be in the range of 92.6–97.8%. The latter high ratios might be ascribed to the presence of the cyclic amide function in structure of these dyestuffs.

Keywords: Degree of exhaustion; synthesis; tartrazine dye analogues

Since Ludwig Knorr's report[1] in 1883 for preparation of Developer Z (3-methyl-1-phenyl-5-pyrazolone) and Ziegler's discovery[2] in 1887 of the yellow dyestuff tartrazine i.e., 1-(*p*-sulphophenyl)-4-(*p*-sulphophenylazo)pyrazol-5-one 3-carboxylic acid, numerous pyrazol-4- or -5-one derivatives have been synthesized[3,4] and widely used in the fields of photography and textile dyeing.[5–7] Such compounds provide a fairly full range of hues, especially yellows, oranges, and and reds. They also have very high all-round fastness properties, in particular toward light, heat, water, acids, and alkalies.

In view of these findings and the current interest in utilizing the arylazo-4-pyrazolone dyestuffs of type (A) for dyeing different types of fibers, the present investigation describes the synthesis of a novel group of tartrazine dyes analogous of type (B).

EXPERIMENTAL

All melting points are uncorrected and measured on a Griffin & George MBF 010T apparatus. Recorded yields correspond to the pure products.

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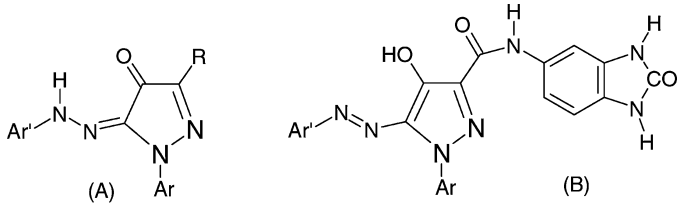


Ar and Ar' = sulphoaryl groups

IR (KBr) spectra were recorded on a Perkin Elmer SP-880 spectrophotometer and ^{1}H NMR spectra were measured on a Varian 270 MHz spectrometer using $CDCl_3$ as a solvent and trimethylsilane (TMS) as an internal standard (chemical shifts are given as δ in ppm). Microanalyses were carried out in the Microanalytical Data Unit in Cairo and at El-Mansoura University.

Synthesis of 4-Bromo-2,3-dioxo-N-(2′-oxobenzimidazol-5′-yl)butyramide (II)

Benzimidazol-5-yl acetoacetamide derivative I[8] (0.05 mmol, 11.66 g) was dissolved in 40 ml of chloroform, and the solution was gradually treated, with occasional shaking, with bromine (0.05 mmol, 2.60 ml) in 20 ml of chloroform. The mixture was left overnight. The precipitated product was filtered off and recrystallized from petroleum ether (60/80) to give yellowish orange crystals of melting point 178°C (46%).

Analysis for $C_{11}H_{10}N_3O_3Br$ (312.15)
Calcd: C, 42.32%, H, 3.24%, and N, 13.47%.
Found: C, 42.46%, H, 3.11%, and N, 13.26%.

IR Spectra (ν/ cm^{-1}): 3310 (intramolecular hydrogen bonded NH), 3180 (free NH), 3060 (CH stretching), 2965–2905 (CH_2 grouping), 1765 (bromoacetyl CO), 1680 (cyclic amide I band) and 1645 (acyclic amide band).

The ^{1}H-NMR spectrum of this compound ($CDCl_3/\delta$ in ppm): 8.10–7.20 (multiplet, 3H, aromatic protons), 5.80–5.20 (broad, 3H, cyclic & acyclic amidic NH), 4.00 (singlet, 2H, CO—CH_2—CO), and 3.94 (singlet, 2H, Br—CH_2—CO).

Synthesis of 4-Bromo-2,3-dioxo-N-(2′-oxobenzimidazol-5′-yl)butyramide 2-sulphoarylhydrazone derivatives (IIIa–e)

An aryl sulphonic acid (0.05 mmol, 10.5 g) was mixed, in a 250 ml conical flask, with anhydrous sodium carbonate (2.65 g) and water

(100 ml), and the whole mixture was warmed until a clear solution was obtained and then it was cooled to about 15°C. A solution of sodium nitrite (0.052 mmol, 3.6 g) in water (10 ml) was added. The resulting solution was slowly added with stirring into a 600 ml beaker containing concentrated hydrochloric acid (10.5 ml) and crushed ice (60 gm). The solution was tested for the presence of free nitrous acid and kept stirred for 15 min whereupon fine crystals of the diazoarylsulphonate soon separated. The suspension was kept in an ice water bath for 10 min and then poured, with stirring, into a solution of the bromo-acetoacetamide derivative (II) (0.05 mmol, 15.60 g) in cold 10% sodium hydroxide solution (50 ml). The whole mixture was cooled to 0–3°C. Coupling takes place readily and the dyestuff separates as a paste. The whole mixture was stirred well for 10 min and warmed until the paste was dissolved completely, and concentrated sodium chloride solution (20 ml) was added to that mixture. The solution was allowed to cool spontaneously for 1 h in air and then was cooled in an ice bath until complete precipitation of the product occured. The salt was collected by filtration, washed with a little saturated sodium chloride solution and dried at 80°C. Acidification of aqueous solution of the salt gave the pure 4-bromro-2,3dioxbuteranilide 2-sulphoaryl hydrazone derivatives (IIIa–e) as yellowish white to yellow colored crystals which were recrystallized from ethanol in good yield. Physical properties of the isolated 4-bromo-2,3-dioxobutyramide 2-sulphoaryl hydrazone derivatives (IIIa–e) are listed in Table I.

The IR spectrum (ν-/ cm^{-1}) of compound (IIIa), as a representative example for this series, showed characteristic bands at: 3360 (OH of sulphonic acid moiety), 3230, 3095 (amide and hydrazone NH), 1680 (cyclic amide I band), 1635 (acyclic amide I band), 1630 (bromoacetyl CO), 1600 (C=C of phenyl ring), 1525 (amide II band), and 1345, 1155 (asymmetric and symmetric stretching vibrations of sulphonic acid moiety).

The ^{1}H-NMR spectrum ($CDCl_3/\delta$ in ppm) of the same compound revealed signals at: 13.40 (broad hump, 1H, NH of hydrazone moiety), 12.35 (broad, 1H, SO_3H proton), 8.10–7.65 (multiplet, 7H, aromatic protons), 5.80 (broad hump, 3H, amidic NH protons), and 4.75 (singlet, 2H, bromoacetyl protons).

Synthesis of 4-Hydroxy-1-sulphoarylpyrazole 3-[N(2′-oxo-benzimidazol-5′-yl)]carboxamide Derivatives (IVa–e)

To a mixture of III (0.003 mmol in each case) in n-propanol (15 ml) was added sodium acetate trihydrate (1.5 g) in water (20 ml), and the mixture was refluxed for 3 h and left to cool. During the reflux time, the

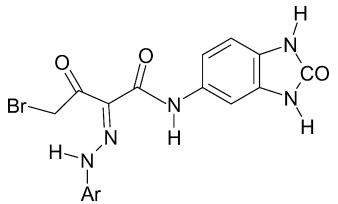


TABLE I 4-Bromo-2,3-dioxobutyranilide-2-sulphoaryl hydrazone Derivatives (IIIa–e)

No.	Ar	Molecular Formula (M.wt)	Colour of the crystals (yield %)	m.p. (°C)	Calculated/Found %		
					C	H	N
IIIa	4-sulphophenyl	$C_{17}H_{14}N_5O_6SBr$	Yellowish white	107	41.14	2.85	14.11
		(496.32)	67		41.43	3.01	13.99
IIIb	2-carboxy-4-sulphophenyl	$C_{18}H_{14}N_5O_8SBr$	Yellowish white	123–124	40.01	2.62	12.96
		(540.34)	68		40.06	2.83	12.74
IIIc	2,5-dichloro-4-sulphophenyl	$C_{17}H_{12}N_5O_6SBrCl_2$	Yellowish white	179	36.12	2.14	12.39
		(565.21)	70		36.58	2.23	12.01
IIId	8-sulphonaphthyl	$C_{21}H_{16}N_5O_6SBr$	Yellow	162–163	46.16	2.96	12.82
		(546.39)	72		45.95	3.12	13.11
IIIe	6-sulphonaphthyl	$C_{21}H_{16}N_5O_6SBr$	Yellow	158–159	46.16	2.96	12.82
		(546.39)	73		46.22	2.68	13.01

color of the reaction mixture changed from yellow to brownish green. The colored solid that separated was collected, washed several times with water, and finally recrystallized from ethanol or acetic acid to give the pure product (69–81%). Physical data of the isolated 4-hydroxy-1-sulphoarylpyrazole 3-carboxamide derivatives (IVa–e) are listed in Table II.

The IR spectrum (ν/ cm^{-1}) of compound (IVa), as a representative example for this series, revealed characteristic bands at: 3355 (OH of sulphonic acid function), 3325 (enolic OH function), 3195 (amidic NH), 1675 (cyclic amide I band), 1650 (acyclic amide I band), 1615 (C=N),1595 (C=C), 1530 (amide II band), and 1350, 1145 (asymmetric and symmetric stretching vibrations of sulphonic acid moiety).

Synthesis of 4-Hydroxy-1-sulphoaryl-5-sulphoarylazo-pyrazole 3-[N-(2′-oxo-benzimidazol-5′-yl)]carboxamide Derivatives V–IX(a–e)

An aryl sulphonic acid derivative (0.03 mmol in each case), was dissolved with stirring in sodium hydroxide solution (100 ml, 0.03 M). To this solution was added sodium nitrite solution (7.5 ml, 4 M), and the whole mixture was slowly poured into a mixture of hydrochloric acid (12 ml, 30%) and ice (50 g) and kept stirred for 3 h at 0–5°C. The produced diazonium salt solution was added slowly (over 30 min), with stirring, to a mixture of the 4-hydroxy-1-sulphophenylpyrazole derivative (IVa) (0.03 mmol) and sodium carbonate (6.5 g) in water (140 ml) and left with continuous stirring for further 3 h. The precipitated solid material was collected by filtration, washed several times with concentrated sodium chloride solution, filtered off, and allowed to dry in air. Acidification with dilute acetic acid afforded the crude product which was recrystallized from acetic acid to give highly colored crystals of the required dyestuffs Va–e in high yield. Similarly, the other four series of 5-sulphoarylazo-1-sulphoaryl pyrazole derivatives were prepared. These dyes together with their physical data are listed in Tables III–VII.

The IR spectrum of compound Va (ν-/cm^{-1}), as a representative example for these dyes, showed characteristic bands at: 1680 (cyclic amide I band), 1635 (acyclic amide I band), 1530 (amide II band), 1455 (N=N azo function), 1340 and 1150 (asymmetric and symmetric stretching vibrations of SO_3H group).

The ^{1}H-NMR spectrum ($CDCl_3$/δ in ppm) of compound Vc revealed signals at: 5.75 (broad hump, 3H, amidic NH protons), 8.20–7.10 (multiplet, 11 H, aromatic protons), 9.45 (broad, 1H, enolic OH), and 12.50 (broad, 2H, of the two sulphonic acid mieties).

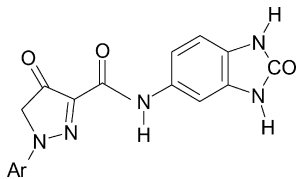


TABLE II 4-Hydroxy-1-sulphoaryl-3-[N-(2′-oxobenzimidazol-5′-yl)carboxamide] Pyrazole Derivatives (IVa–e)

No.	Ar	Molecular Formula (M.wt)	Color of crystals (yield %)	m.p. (°C)	Calculated/Found %		
					C	H	N
IVa	4-sulphophenyl	$C_{17}H_{13}N_5O_6S$	Orange	112	49.15	3.16	16.86
		(415.41)	(69)		48.98	3.21	16.51
IVb	2-carboxy-4-sulphophenyl	$C_{18}H_{13}N_5O_8S$	Yellowish orange	144–145	47.05	2.86	15.25
		(459.42)	(71)		46.88	2.97	15.5
IVc	2,5-dichloro-4-sulphophenyl	$C_{17}H_{11}N_5O_6SCl_2$	Orange	168–169	42.16	2.29	14.47
		(484.29)	(74)		42.40	2.41	14.31
IVd	8-sulphonaphthyl	$C_{21}H_{15}N_5O_6S$	Orange	196–197	54.18	3.26	15.05
		(465.47)	(81)		53.89	3.22	15.11
IVe	6-sulphonaphthyl	$C_{21}H_{15}N_5O_6S$	Orange red	179–181	54.18	3.26	15.05
		(465.47)	(79)		54.36	3.38	15.00

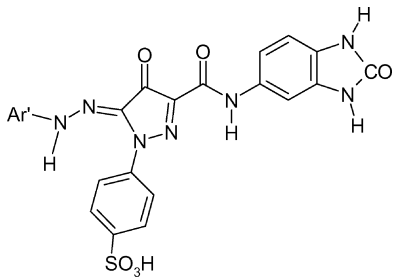


TABLE III 5-Sulphoarylazo-1-sulphophenyl-4-hydroxy-3- [N-(2′-oxobenzimidazol-5′- yl)-carboxamide] Pyrazole Derivatives (Va–e)

No.	Ar	Molecular Formula (M.wt)	Color of crystals (yield %)	m.p. (°C)	Calculated/Found %		
					C	H	N
Va	4-sulphophenyl	$C_{23}H_{17}N_7O_9S_2$	Yellow	131–132	46.07	2.86	16.36
		(599.59)	71		45.89	2.93	16.27
Vb	2-carboxy-4-sulphophenyl	$C_{24}H_{17}N_7O_{11}S_2$	Orange	139–140	44.78	2.67	15.24
		(643.60)	74		44.92	2.74	14.96
Vc	2,5-dichloro-4-sulphophenyl	$C_{23}H_{15}N_7O_9S_2Cl_2$	Orange red	203–204	41.32	2.27	14.67
		(668.47)	77		41.60	2.35	14.56
Vd	8-sulphonaphthyl	$C_{27}H_{19}N_7O_9S_2$	Red	277	49.91	2.95	15.10
		(649.65)	81		49.76	3.08	15.16
Ve	6-sulphonaphthyl	$C_{27}H_{19}N_7O_9S_2$	Red 86	246–247	49.91	2.95	15.10
		(649.65)	86		49.97	2.68	15.06

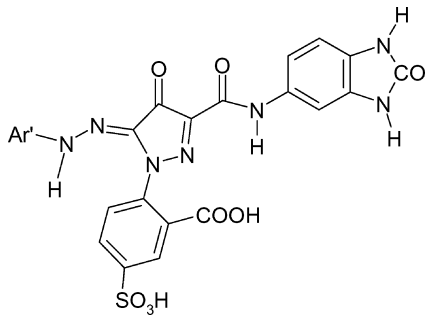


TABLE IV
5-Sulphoarylazo-1-(2′-carboxy-4′-sulphophenyl)-4-hydroxy-3-[N-(2′-oxobenzimidazol-5′yl)carboxamide] Pyrazole Derivatives (VIa–e)

No.	Ar	Molecular Formula (M.wt)	Color of crystals (yield %)	m.p. (°C)	Calculated/Found %		
					C	H	N
VIa	4-sulphophenyl	$C_{24}H_{17}N_7O_{11}S_2$	Reddish orange	184–185	44.78	2.67	15.24
		(643.6)	72		44.81	2.82	15.60
VIb	2-carboxy-4-sulphophenyl	$C_{25}H_{17}N_7O_{13}S_2$	Red	161–162	43.67	2.50	14.26
		(687.61)	75		44.01	2.37	14.43
VIc	2,5-dichloro-4-sulphophenyl	$C_{24}H_{17}N_7O_{11}S_2Cl_2$	Red	173–174	40.46	2.13	13.76
		(712.48)	78		40.66	2.15	14.06
VId	8-sulphonaphthyl	$C_{28}H_{19}N_7O_{11}S_2$	Dark red	279–280	48.48	2.77	14.14
		(693.66)	82		48.31	2.86	14.31
VIe	6-sulphonaphthyl	$C_{28}H_{19}N_7O_{11}S_2$	Blue	244–245	48.48	2.77	14.14
		(699.66)	85		48.22	2.92	14.07

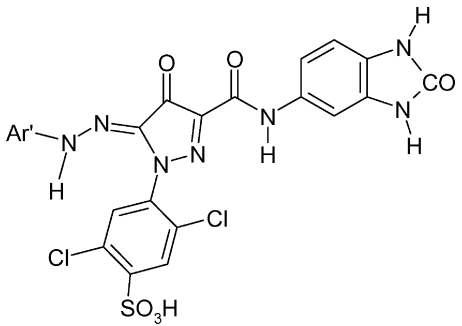


TABLE V 5-Sulphoarylazo-1-(2′,5′-dichloro-4′-sulphophenyl)-4-hydroxy-3-[N-(2′-oxobenzimidazol- 2′- yl) carboxamide] Pyrazole Derivatives (VIIa–e)

No.	Ar	Molecular Formula (M.wt)	Color of crystals (yield %)	m.p. (°C)	Calculated/Found % C	H	N
VIIa	4-sulphophenyl	$C_{23}H_{15}N_7O_9S_2Cl_2$ (668.47)	Orange 71	211–212	41.32 41.28	2.27 2.41	14.67 14.78
VIIb	2-carboxy-4-sulphophenyl	$C_{24}H_{15}N_7O_{11}S_2\ Cl_2$ (712.48)	Red 75	189–191	40.46 40.09	2.13 2.16	13.77 13.85
VIIc	2,5-dichloro-4-sulphophenyl	$C_{23}H_{13}N_7O_9S_2\ Cl_4$ (737.35)	Red 77	236–237	37.46 37.71	1.78 1.93	13.30 13.11
VIId	8-sulphonaphthyl	$C_{27}H_{17}N_7O_9S_2\ Cl_2$ (718.53)	Blue 83	256–258	45.13 44.98	2.39 2.14	13.65 13.78
VIIe	6-sulphonaphthyl	$C_{28}H_{17}N_7O_9S_2\ Cl_2$ (718.53)	Blue 86	230–231	45.13 45.26	2.39 2.19	13.65 13.80

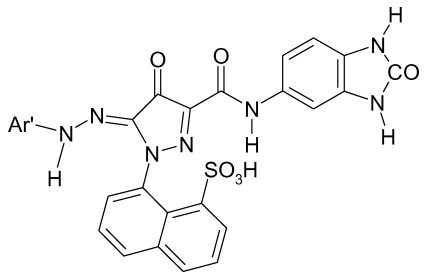


TABLE VI 5-Sulphoarylazo-1-(8′-sulphonaphthyl)-4-hydroxy-3-[N-(2′-oxobenzimidazol-5′-yl)-carboxamide] Pyrazole Derivatives (VIIIa–e)

No.	Ar	Molecular Formula (M.wt)	Color of crystals (yield %)	m.p. (°C)	Calculated/Found %		
					C	H	N
VIIIa	4-sulphophenyl	$C_{27}H_{19}N_7O_9S_2$	Orange	161–162	49.92	2.95	15.09
		(649.65)	72		50.15	2.98	14.86
VIIb	2-carboxy-4-sulphophenyl	$C_{28}H_{19}N_7O_{11}S_2$	Red	209–211	48.48	2.77	14.14
		(693.66)	75		48.31	2.96	14.02
VIIIc	2,5-dichloro-4-sulphophenyl	$C_{27}H_{17}N_7O_9S_2\ Cl_2$	Red	232–234	45.14	2.39	13.65
		(718.53)	79		45.01	2.41	13.87
VIIId	8-sulphonaphthyl	$C_{31}H_{21}N_7O_9S_2$	Blue	273–274	53.21	3.03	14.02
		(699.71)	84		53.46	2.89	14.26
VIIIe	6-sulphonaphthyl	$C_{31}H_{21}N_7O_9S_2$	Dark blue	259–260	53.21	3.03	14.02
		(699.71)	85		53.17	3.00	13.86

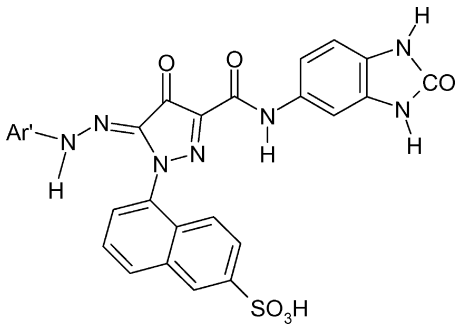


TABLE VII 5-Sulphoarylazo-1-(6′-sulphonaphthyl)-4-hydroxy-3-[N-(2′-oxobenzimidazol-5′-onyl)-carboxamide] Pyrazole Derivatives (IXa–e)

No.	Ar	Molecular Formula (M.wt)	Color of crystals (yield %)	m.p. (°C)	Calculated/Found %		
					C	H	N
IXa	4-sulphophenyl	$C_{27}H_{19}N_7O_9S_2$	Orange	210–212	49.92	2.95	15.09
		(649.65)	71		50.16	2.81	15.03
IXb	2-carboxy-4-sulphophenyl	$C_{28}H_{19}N_7O_{11}S_2$	Scarlet red	189–190	48.48	2.77	14.14
		(693.66)	75		48.62	2.91	14.25
IXc	2,5-dichloro-4-sulphophenyl	$C_{27}H_{17}N_7O_9S_2\ Cl_2$	Navy blue	193–194	45.14	2.39	13.65
		(718.53)	79		45.36	2.48	13.82
IXd	8-sulphonaphthyl	$C_{31}H_{21}N_7O_9S_2$	Blue	225–227	53.21	3.03	14.02
		(699.71)	84		53.26	2.81	13.89
IXe	6-sulphonaphthyl	$C_{31}H_{21}N_7O_9S_2$	Dark blue	207–208	53.21	3.03	14.02
		(699.71)	86		52.98	3.12	14.29

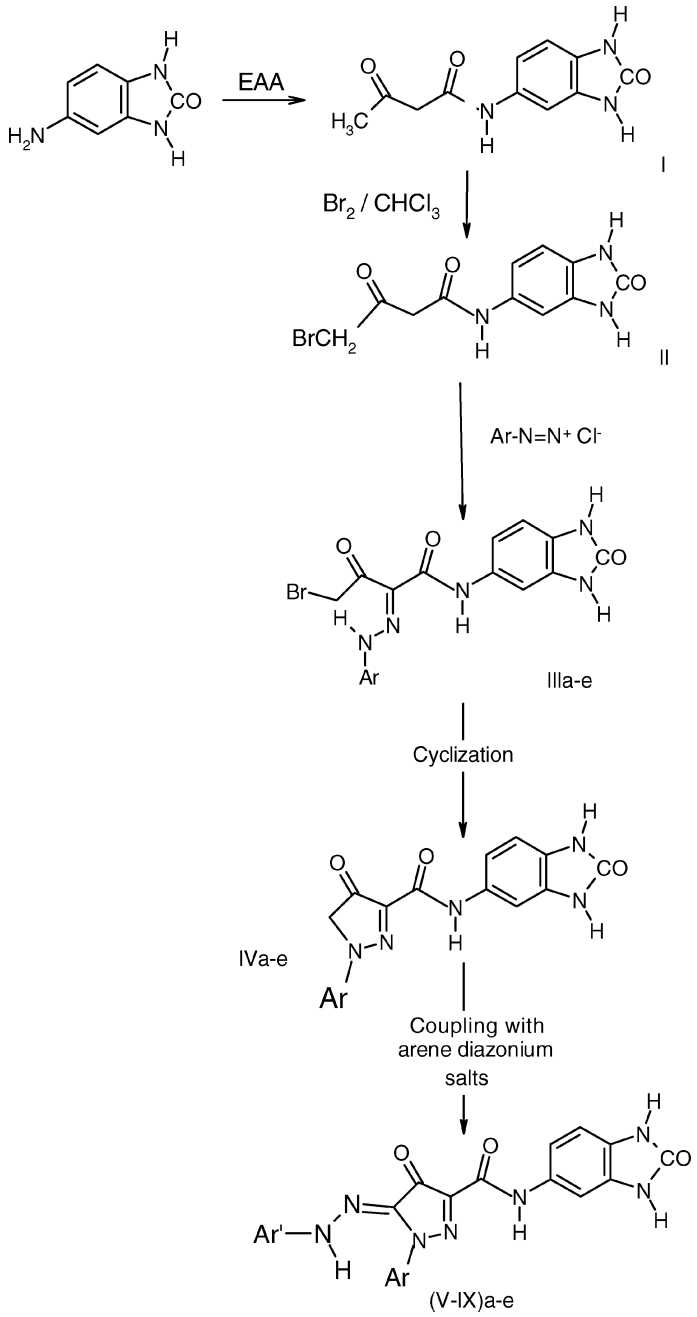
RESULTS AND DISCUSSION

Synthesis of the prepared sulphoarylazo dyestuffs was accomplished according to the sequence of reactions that are given in Scheme 1. Acetoacetanilides were reported[3] to show the carbonyl bands near 1725 and 1660 cm^{-1}. These bands were assigned to the acetyl and amidic carbonyl groups respectively. By analogy, the strong band at 1765 cm^{-1} in the IR spectrum of the hitherto prepared amide derivative II is assigned to the carbonyl group of the bromoacetyl function, whereas, the band at 1680 and 1645 cm^{-1} are assigned to the cyclic and acyclic amide I bands. The higher frequency of the CO stretching vibrations of compound II as compared to that of acetoacetanilide might be attributed to the inductive effect of the bromine atom. The appearance of the ketonic CO band as well as the absence of any enolic OH stretching vibrations indicate that 4-bromo-N-(2′-oxobenzimidazol-5′-yl)-3-oxobutyramide (II), under the condition of measurements, exists almost entirely in the keto form. This is also substantiated from its ^{1}H-NMR spectrum where the signals due to vinylic OH and CH protons were not observed.

The produced 4-bromo-3-oxobutyranilide (II) reacted with diazotized sulpho-aryl amines to yield the corresponding 4-bromo-2,3-dioxobutyramide 2-sulphoarylhydrazone derivatives (IIIa–e) in an overall good yield. Each of these products exhibited a strong band in the region of 1595–1610 cm^{-1} which was assigned to the skeletal C=C in plane vibrations of phenyl moieties.[9]

Solid 2,3-dioxobutyranilide 2-sulphophenyl hydrazone and ethyl 2,3-dioxobutyrate 2-sulphophenylhydrazone were found to exhibit their acetyl CO stretching near 1623 and 1620 cm^{-1} respectively.[10] As to the diazonium coupling products in this study, each exhibits three CO bands: two strong bands near 1680 abd 1635 and a relatively weak one near 1630 cm^{-1}. These were assigned to the cyclic, acyclic amide, and bromoacetyl carbonyl functions, respectively, in agreement with those reported for 2,3-dioxobutyranilide-2-phenylhydrazone.[10] The extremely low value of 1630 cm^{-1} for the bromoacetyl CO indicates the presence of α,β-unsaturation. It also indicates that the acetyl CO group of such coupling product is hydrogen bonded, since the value of 1630 cm^{-1} is still lower than the normal conjugated carbonyl compounds. Both factors, conjugation with C=C or C=N and intramolecular hydrogen bonding, were reported to diminish considerably the force constant of CO groups.[11] Such IR data eliminate the possibility of the presence of compounds IIIa–e in the azo forms. However, it highly substantiate the hydrazone structure for such products.

Furthermore, the spectra of compounds (IIIa–e), show strong and well defined absorption bands near 1345 and 1155 cm^{-1} (for asymmetric



SCHEME 1 Ar & Ar′ = Sulphoaryl moieties (For Ar & Ar′ see Tables I–VII).

and symmetric stretching vibrations of sulphonic acid moiety). Moreover the spectra revealed a strong band near 1560 cm^{-1}, which was not observed in the spectrum of the parent 4-bromo-3-oxobutyramide. Though probably it represents an aromatic ring absorption, the 1560 cm^{-1} band was assigned to the C=N double bond. The fact that the latter does sometimes fall below 1600 cm^{-1} has been reported[12] previously. The low frequency position for the C=N bands of the compound (IIa–e), may be attributed to its conjugation with CO group.[13]

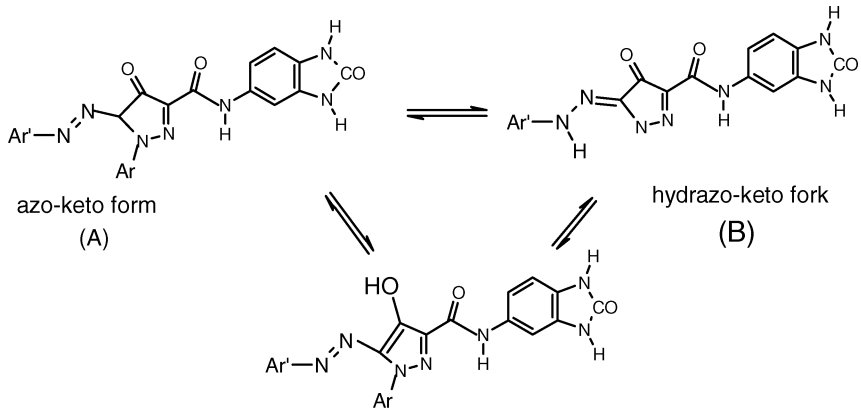
Refluxing ethanolic solution of 4-bromo-2,3-dioxo-N-(2′-oxobenzimidazol-5′-yl)butyramide-2-sulphoaryl hydrazone (IIIa–e) in presence of sodium acetate, afforded the pure crystalline 4-hydroxy-1-sulphoaryl-3-[N-(2′-oxobenzimidazol-5′yl)] carboxamide pyrazole derivatives (IVa–e) (Scheme 1).

The IR spectra of compounds (IV) in potassium bromide possessed an absorption band typical of a sulphonic OH function near 3355 cm^{-1} and an intra-molecularly bonded enolic OH near 3325 cm^{-1}. This suggests that the cyclized products exist in the hydroxy form rather than in the tautomeric keto structure.

The assignment of the hydroxy structure is further substantiated by the fact that each of the compounds IVa–e shows two absorption bands near 1675 and 1650 cm^{-1}, typical of cyclic and acyclic amidic CO functions respectively. As for the 4-oxo structure, if it were present one would expect to find, in the spectra of such compound, three CO absorption bands corresponding to the cyclic, acyclic amide, and ketonic CO groups. In no case could the keto CO band be identified. The complete absence of a cyclic ketonic CO band apparently is compatible with the hydroxy structure.

The ^{1}H-NMR spectral data, in deutereochloroform, are consistent with the assigned 4-hydroxy form of the prepared compounds IVa–e. For example the ^{1}H-NMR spectra of compound (IVa) in $CDCl_3$ showed no signal due to the methylene proton resonance of the keto structure. This result finds support from the previously reported work,[14] on the ^{1}H-NMR spectra of 1-p-tolyl-2-pyrazolin-4-one-3-carboxanilide derivative in trifluoro-acetic acid (TFA) which is known to favor the keto form. The latter spectra revealed two signals at $\delta = 8.30$ and $\delta = 2.30$, assignable to vinylic C=CH and methylene CH_2 proton at C5 of the hydroxy and the keto forms, respectively. On the basis of their integrated areas, the percentage of the hydroxy form was calculated to be 75%.

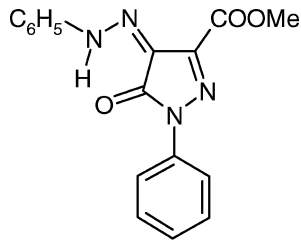
Treatment of the pyrazole derivatives IVa–e with sulphoaryl diazonium salts in alkaline medium afforded the corresponding 5-sulphoarylazo derivatives. The resulting coupling products V–IX(a–e) can exist in three tautomeric forms: the azo-keto form (A), the hydrazo-keto form (B) and the hydroxy-azo form (C) (Scheme 2). In the present



SCHEME 2

investigation, the latter hydroxy-azo tautomeric structure (C) has been found to represent the actual structure of these compounds. The spectral evidence on which such a conclusion is based involved IR and ^{1}H-NMR spectra.

Concerning IR spectra, it has been showed that 3-carboxy derivatives of 4-arylazo-2-pyrazolin-5-ones have the hydrazone structure. For example, 1-phenyl-3-methoxycarbonyl-4-phenylhydrazono-2-pyrazolin-5-one derivative (VI) exhibits two carbonyl absorption bands at 1735 and 1665 cm^{-1}. These were assigned to the ester and lactam CO groups respectively.[15]

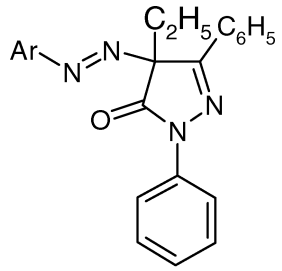


(VI)

In our case, the carbonyl region of IR spectra of each of the prepared dyestuffs (V–IX), however, revealed only two sharp and well defined carbonyl peaks near 1680 $\pm$ 5 and 1635 cm^{-1}. If the hydrazo-keto form (B) represented the actual structure of these coupling products, one

would expect three carbonyl bands to appear, the absence of acyclic ketonic band in this region thus exclude the possibility of structures of type A or B.

In the spectra of each of the examined 4-pyrazolone dyestuffs (V–IX), two other absorption bands were noted, one intense band in the region 1530 cm^{-1} and the second in the region of 1460-1440 cm^{-1}. As the former band was observed in the spectra of both 1-sulphoaryl-4-hydroxypyrazole-3-carboxamides (IVa–e) and the coupling products of 4-bromo-3-oxobutyramides (IIIa–e), it was not assigned to an azo, but to the amidic group (amide II band) which is common in all the three series of compounds. Such an assignment is reinforced by the fact that in the spectra of 1,3-diphenyl-4-ethyl-4-arylazo-2-pyrazolin-5-one (VII), which does contain an azo group,[16] the band near 1530 cm^{-1} definitely vanished in the solid state and in chloroform solution. On the other hand, amides are known to exhibit their CONH band (amide II) in the region 1570–1555 cm^{-1} regions.[17]



(VII)

Regarding the 1460-1440 cm^{-1} band, it was absent in the spectra of both the parent 4-pyrazolones (IVa–e) and in the coupling products of 4-bromo-3-oxobutyranilide IIIa–e. It was therefore assigned to an azo group. Since the coupling products of 5-pyrazolone, which are known to exist in the hydrazone form, do not exhibit such a band, it is not unreasonable to conclude, therefore, that the hitherto prepared 4-sulphoarylazo-pyrazolone dyestuffs do exist in the azo forms (A or C). As the ^{1}H-NMR spectrum provides strong evidence against the presence of methine (CH) proton, it would not be unreasonable to exclude structure (A). This elimination is compatible with the absence of a ketonic CO band. In consequence the tautomeric structure (C) of 5-sulphoarylazo derivatives of the 4-hydroxy-1-sulphoarylpyrazole 3-carboxamides, under investigation, is the only one which accommodates these IR observations.

The ^{1}H-NMR spectra of the prepared dyestuffs in $CDCl_3$, showed the usual phenyl pattern, a multiplet at δ 7.10–8.20 and two broad acidic proton peaks at δ 9.40 $\pm$ 0.20 and at δ 12.30 $\pm$ 0.30, assignable to an intramolecularly hydrogen bonded hydroxy proton and the acidic protons of sulphonic acid moieties in these compounds. Another small hump near δ 5.70 $\pm$ 0.20 was observed in the spectra and was attributed to the amidic NH protons. Judging from these results, it could be concluded that the diazonium coupling products (V–IX) exist predominantly in hydroxy-azo form.

DYEING PERFORMANCE

The degree of exhaustion of the hitherto synthesized 3-[2-(oxoimidazo-5-yl) carboxamido] tartrazine dye analogues was determined colorimetrically and found to be in the range of 92.6–97.8%. The latter high ratios might be ascribed to the presence of the cyclic amide function in structure of these dyestuffs.

The importance of the cyclic amide function might be explained on the basis of the fact that in the process of bonding of the dye with the

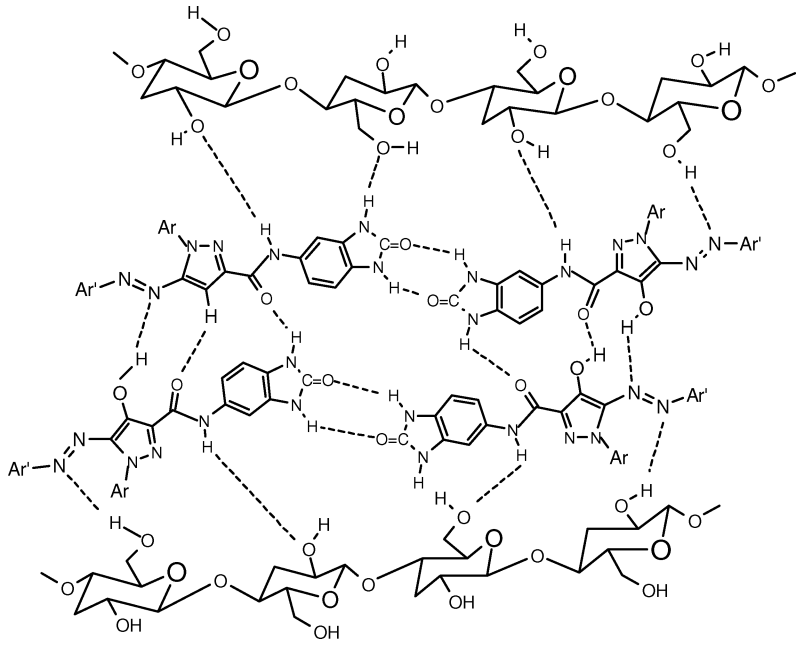


FIGURE 1 Tartrazine Dye Analogues.

fiber, two different bonds via NH or oxygen moieties play a significant role. They probably form the dimers of the dye as well as dye-fiber bonds.

A highly probable mode of binding with cellulose molecules of the fiber comprises the formation of a dimer by one of the NH groups, while the second NH group shared in the formation of the bond between the dimer and cellulose fiber (Figure 1). Such a proposition makes it possible to explain the particularly good affinity of these dyestuffs to the fiber, which ensures an uninterrupted interaction of the two NH groups, forming various types of association. Further binding of the previously mentioned dimers might be ascribed to the presence of the hydroxy azo moiety in these dyestuffs (Figure 1). The behavior of the hitherto prepared dyestuffs (V–IX) toward cellulosic fibers finds support from previous reports in literature.[18]

Assessment of the dyeing performance together with evaluation of the percentage reflectance of the dyed fiber, at different wavelengths in the visible region, and application of Kubelka-Munk equation for calculation of K/S function of the dyed materials are, for the time being, under investigation and will be published separately.

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