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Synthesis and Dyeing Characteristics of Some New Asymmetrical 3-Cyanoformazans

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ABSTRACT

A series of new asymmetrical 3-cyanoformazans have been synthesised by coupling diazotised 5-amino-3-phenylpyrazole and 3-aminobenzimidazole with cyanoacetanilide and treatment of the resulting azo derivatives with arene diazonium salts. The behaviour of the newly synthesised formazans as direct, acid and basic dyes is reported.

1 INTRODUCTION

Whilst an extensive number of formazans have been reported in the literature[1–3] few data have appeared concerning the synthesis of asymmetrical formazans bearing heterocyclic moieties or on the use of such formazans as dyes. In the course of our investigations on the reactions of activated nitriles,[4–7] we felt it of interest to investigate the synthesis and dyeing properties of some asymmetrical 3-cyanoformazans. These new formazans bear imino functions and appear to be interesting as dyes capable of hydrogen bonding with various polymers.

2 RESULTS AND DISCUSSION

Diazotised 5-amino-3-phenylpyrazole (**Ia**) and 2-aminobenzimidazole (**Ib**) coupled with cyanoacetanilide (**II**) in sodium acetate buffered solution to

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TABLE 1
Characterization Data for Compounds III and IV

Compound	*M.p. (°C)*	*Yield (%)*	*Mol. formula*	*Analysis (%):*		*Found Calcd*
				C	*H*	*N*
IIIa	196	81	$C_{18}H_{14}N_6O$	66·3	4·1	25·3
				66·4	4·3	25·4
IIIb	162	79	$C_{16}H_{12}N_6O$	62·9	4·0	27·5
				63·15	4·0	27·6
IVa	220	73	$C_{17}H_{13}N_7$	64·8	4·3	31·1
				64·75	4·15	31·1
IVb	238	69	$C_{18}H_{15}N_7$	65·8	4·7	29·6
				65·6	4·6	29·8
IVc	258–260	73	$C_{17}H_{12}N_7Br$	52·0	2·9	24·7
				51·8	3·7	24·9
IVd	240	80	$C_{17}H_{12}N_8O_2$	56·8	3·2	31·3
				56·7	3·4	31·1
IVe	251	76	$C_{17}H_{13}N_7O$	61·5	4·1	29·3
				61·6	3·95	29·6
IVf	224	80	$C_{18}H_{13}N_7O_2$	60·3	3·5	27·4
				60·2	3·65	27·3
IVg	272–274	79	$C_{15}H_{11}N_7$	62·4	3·9	33·8
				62·3	3·8	33·9
IVh	286–290	68	$C_{16}H_{13}N_7$	63·4	4·2	32·4
				63·35	4·3	32·3
IVi	231	61	$C_{15}H_{10}N_7Br$	49·0	2·6	26·8
				48·9	2·7	26·6
IVj	193	83	$C_{15}H_{10}N_8O_2$	53·9	3·3	33·7
				53·9	3·1	33·5
IVk	>300	68	$C_{15}H_{11}N_7O$	59·10	3·5	32·2
				59·01	3·6	32·1
IVl	223	73	$C_{16}H_{11}N_7O_2$	57·5	3·2	29·4
				57·7	3·3	29·4

give the azocyanoacetanilide derivatives **IIIa** and **IIIb** respectively. Although the method of formation of the products by an azo coupling reaction points to them having an azo structure, spectral data[8] indicate them to have a hydrazone configuration. The reaction between arene diazonium ions and the azocyanoacetanilide derivatives **IIIa** and **IIIb** in the presence of sodium hydroxide (and not in the presence of sodium acetate) produced the 3-cyanoformazan derivatives **IV**. This result indicates that the phenylcarbamoyl group undergoes hydrolytic cleavage during this coupling reaction. The newly synthesised formazans (Scheme 1) were all intensely coloured and relevant characterisation data are shown in Tables 1–3.

TABLE 2
Spectroscopic Data for Compounds **III** and **IV**

Compound	*IR spectra, selected bands* (cm^{-1})	^1H-*NMR*, δ (*ppm*)
IIIa	3 369, 3 320, 3 225 (NH); 2 220 (CN); 1 678 (CO); 1 620 (C=N); 1 590 (C=C)	4·1 (s, 1H, NH); 6·4 (s, 1H, pyrazole H-4); 7·1–7·5 (m, 11H, aromatic and NH); 9·9 (s, 1H, NH)
IIIb	3 336, 3 279 (NH); 2 220 (CN); 1 680 (CO); 1 620 (C=N); 1 600 (C=C)	3·9 (s, 1H, NH); 7·4–7·7 (m, 10H, aromatic and NH); 9·7 (s, 1H, NH)
IVa	3 367, 3 226 (NH); 2 222 (CN); 1 632, 1 620, 1 600 (C=N, C=C and N=N)	5·1 (s, 1H, NH); 6·5 (s, 1H, pyrazole H-4); 7·2–7·6 (m, 11H, aromatic and NH)
IVb	3 340–3 290 (NH); 2 222 (CN); 1 640–1 600 (C=N, C=C and N=N)	2·3 (s, 3H, CH_3); 4·1 (s, 1H, NH); 6·4 (s, 1H, pyrazole H-4); 7·3–7·8 (m, 10H, aromatic and NH)
IVc	3 279, 3 247 (NH); 2 227 (CN); 1630–1 600 (C=N, C=C and N=N)	
IVd	3 350–3 280 (NH); 2 222 (CN); 1 630–1 600 (C=N, C=C and N=N)	
IVe	3 500–2 500 (OH and NH); 2 227 (CN); 1 640, 1 620, 1 610 (C=N, C=C and N=N)	5·2 (s, 1H, NH); 6·4 (s, 1H, pyrazole H-4); 7·2–7·7 (m, 10H, aromatic and NH); 9·8 (s, 1H, OH)
IVf	3 500, 337–2 700 (OH and NH); 2 225 (CN); 1 700 (CO); 1 640–1 600 (C=N, C=C and N=N)	4·6 (s, 1H, NH); 6·4 (s, 1H, pyrazole H-4); 7·1–7·6 (m, 9H, aromatic); 12·1–12·5 (s, br, 2H, OH and NH)
IVg	3 360, 3 230 (NH); 2 227 (CN); 1 640, 1 620, 1 600 (C=N, C=C and N=N)	4·1 (s, 1H, NH); 7·3–7·6 (m, 9H, aromatic); 7·9 (s, 1H, NH)
IVh	3 350, 3 260 (NH); 2 222 (CN); 1 635–1 600 (C=N, C=C and N=N)	2·2 (s, 3H, CH_3); 4·6 (s, 1H, NH); 7·2–7·5 (m, 8H, aromatic); 11–12 (s, 1H, NH)
IVi	3 345–3 280 (NH); 2 225 (CN); 1 640–1 600 (C=N, C=C and N=N)	
IVj	3 378, 3 229 (NH); 2 222 (CN); 1 630–1 600 (C=N, C=C and N=N)	
IVk	3 500–2 490 (OH and NH); 2 225 (CN); 1 635, 1 615, 1 600 (C=N, C=C and N=N)	4·4 (s, 1H, NH); 7·3–7·6 (m, 8H, aromatic); 11·2–11·6 (s, br, 2H, OH and NH)
IVl	3 500–2 700 (OH and NH); 2 220 (CN); 1 705 (CO); 1 640–1 600 (C=N, C=C and N=N)	5·1 (s, 1H, NH); 7·2–7·7 (m, 8H, aromatic); 11·9–12·4 (s, br, 2H, OH and NH)

TABLE 3
Electronic Absorption Spectra for Compounds **III** and **IV**

Compound	*Absorption maxima in methanol*					
	λ_{max} *(nm)*	*log* ε	λ_{max} *(nm)*	*log* ε	λ_{max} *(nm)*	*log* ε
IIIa	367	4·33	288	3·75	231	4·26
IIIb	380	4·25	290	3·81	237	4·35
IVa	445	4·46	294	4·12	250	4·02
IVb	461	4·36	299	4·10	240	4·06
IVc	424	4·09	301	4·11	261	3·98
IVd	429	4·20	290	4·13	263	4·21
IVe	436	4·41			246	4·11
IVf	459	4·29	311	4·08	259	4·08
IVg	448	4·44	289	4·10	232	4·10
IVh	457	4·51	295	4·09	229	4·03
IVi	458	4·30	297	4·13	238	4·14
IVj	470	4·29	303	4·06	253	4·28
IVk	449	4·31			249	3·99
IVl	439	4·43	298	4·06	260	4·21

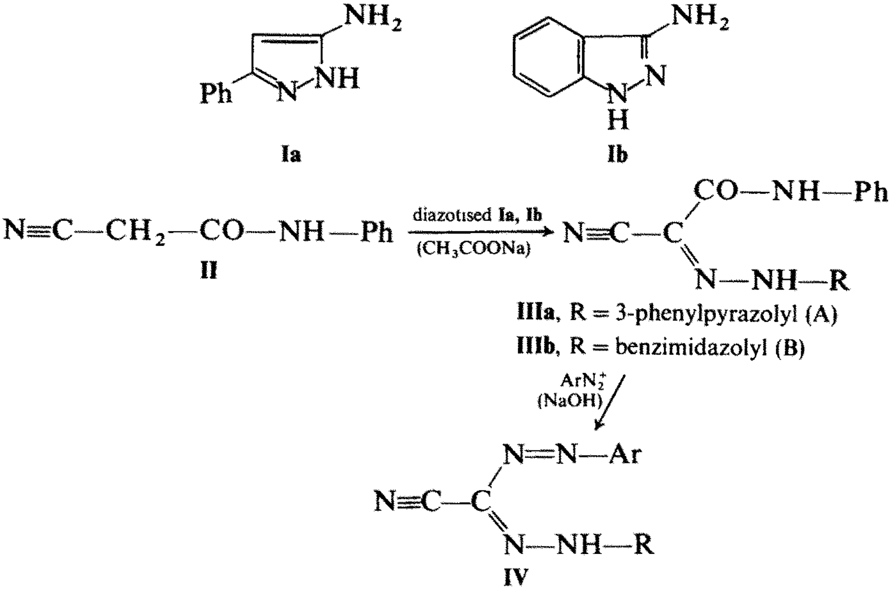
Compounds **III** and **IV** were evaluated as dyes on various substrates. Colouration properties on cellulose, wool and nylon were particularly good. All dyeings (Table 4) had very good fastness to light, although fastness to washing was only moderate.

3 EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were recorded (KBr) on a Pye–Unicam SP1000 spectrophotometer. ^{1}H-NMR spectra were obtained in $(CD_3)SO$ on a Varian EM 390 spectrometer using $SiMe_4$ as internal standard; chemical shifts are expressed as δ values. Microanalyses were performed by the microanalytical centre at Cairo University. Cyanoacetanilide was prepared following the literature procedure.[9]

3.1 Reactions of diazotised Ia and Ib with cyanoacetanilide

A solution of either **Ia** or **Ib**, (0·01 mol) in glacial acetic acid (5 cm^3) and concentrated hydrochloric acid (5 cm^3, 37% by volume) was cooled at 0°C and treated with sodium nitrite (0·7 g dissolved in a minimum amount of water). The solution was stirred for 30 min and added dropwise with stirring



a, $R = A$; $Ar = C_6H_5$
b, $R = A$; $Ar = C_6H_4CH_3\text{-}p$
c, $R = A$; $Ar = C_6H_4Br\text{-}p$
d, $R = A$; $Ar = C_6H_4NO_2\text{-}p$
e, $R = A$; $Ar = C_6H_4OH\text{-}o$
f, $R = A$; $Ar = C_6H_4COOH\text{-}o$
g, $R = B$; $Ar = C_6H_5$
h, $R = B$; $Ar = C_6H_4CH_3\text{-}p$
i, $R = B$; $Ar = C_6H_4Br\text{-}p$
j, $R = B$; $Ar = C_6H_4NO_2\text{-}p$
k, $R = B$; $Ar = C_6H_4OH\text{-}o$
l, $R = B$; $Ar = C_6H_4COOH\text{-}o$

Scheme 1. Synthesis of 3-cyanoformazan derivatives **IV**.

to a cold solution of cyanoacetanilide (0·01 mol) in ethanol (100 cm^3, containing 3 g sodium acetate). The temperature was kept below 5°C during the addition and the reaction liquor was then left to stand overnight in a refrigerator. The resulting precipitate was filtered and washed thoroughly with water and crystallised from ethanol (see Table 1).

3.2 Reactions of IIIa and IIIb with arene diazonium salts

A solution of **IIIa** or **IIIb** (0·01 mol in 50 cm^3 ethanol) was mixed with a cold solution of sodium hydroxide (0·8 g in 50 cm^3 water). The solution was cooled to below 5°C and a solution of the appropriate arene diazonium chloride (prepared from 0·01 mol of the amine and the appropriate quantities of hydrochloric acid and sodium nitrite) was added dropwise with stirring. After addition, the solution was stirred for 20 min and left to stand overnight in a refrigerator. The precipitate was filtered, washed with water and recrystallised from acetic acid.

TABLE 4
Dyeing and Fastness Properties of Compounds **IVa–IVl**

Compound	*Dyeing method*	*Dyeing fabric*	*Shade*	*Fastness properties*[a]	
				Light	*Wash*
IVa	Direct	Cotton	Red	6	3
		Viscose	Red–orange	6	3
		Nylon-6	Light red	6	2
		Wool	Red	6	2–3
	Acid	Nylon-6	Red–orange	6	3
		Wool	Gold red–brown	6	2
	Basic	Acrylic	Light red	6	2
IVb	Direct	Cotton	Light orange	6	3
		Viscose	Orange	6	2–3
		Nylon-6	Orange	6	3
		Wool	Orange	6	2
	Acid	Nylon-6	Orange	6	2
		Wool	Orange	6	3
	Basic	Acrylic	Orange–yellow	6	2–3
IVc	Direct	Cotton	Dark red	6	3
		Viscose	Light brown	6	2
		Nylon-6	Brown	6	2
		Wool	Bright brown	6	2
	Acid	Nylon-6	Golden brown	6	2–3
		Wool	Red brown	6	3
	Basic	Acrylic	Dark brown	6	3
IVd	Direct	Cotton	Red	6	3
		Viscose	Red	6	3
		Nylon-6	Red–Orange	6	3
		Wool	Red	6	2–3
	Acid	Nylon-6	Light red	6	3
		Wool	Red	6	3
	Basic	Acrylic	Orange	6	2
IVe	Direct	Cotton	Brown	6	3
		Viscose	Brown	6	3
		Nylon-6	Brown	6	3
		Wool	Brown	6	3
	Acid	Nylon-6	Brown	6	3
		Wool	Brown	6	3
	Basic	Acrylic	Light brown	6	3
IVf	Direct	Cotton	Light orange	6	3
		Viscose	Light orange	6	2–3
		Nylon-6	Orange	6	3
		Wool	Orange	6	2
	Acid	Nylon-6	Light orange	6	2
		Wool	Light orange	6	2–3
	Basic	Acrylic	Orange	6	3

TABLE 4—*contd.*

Compound	*Dyeing method*	*Dyeing fabric*	*Shade*	*Fastness properties*[a]	
				Light	*Wash*
IVg	Direct	Cotton	Red–brown	6	3
		Viscose	Light brown	6	2
		Nylon-6	Light brown	6	2
		Wool	Brown	6	2
	Acid	Nylon-6	Brown	6	2–3
		Wool	Red–brown	6	3
	Basic	Acrylic	Red–brown	6	3
IVh	Direct	Cotton	Light red	6	3
		Viscose	Light red	6	3
		Nylon-6	Red	6	3
		Wool	Gold–red–brown	6	3
	Acid	Nylon-6	Red–brown	6	2–3
		Wool	Red	6	3
	Basic	Acrylic	Light red	6	3
IVi	Direct	Cotton	Orange	6	3
		Viscose	Orange	6	3
		Nylon-6	Orange	6	3
		Wool	Orange	6	3
	Acid	Nylon-6	Orange	6	3
		Wool	Orange	6	3
	Basic	Acrylic	Orange–yellow	6	3
IVj	Direct	Cotton	Red	6	3
		Viscose	Red	6	2–3
		Nylon-6	Red	6	3
		Wool	Red	6	3
	Acid	Nylon-6	Light red	6	3
		Wool	Red–orange	6	3
	Basic	Acrylic	Orange	6	2
IVk	Direct	Cotton	Brown	6	3
		Viscose	Brown	6	3
		Nylon-6	Brown	6	3
		Wool	Brown	6	3
	Acid	Nylon-6	Brown	6	3
		Wool	Brown	6	3
	Basic	Acrylic	Light brown	6	2
IVl	Direct	Cotton	Red	6	3
		Viscose	Scarlet–red	6	3
		Nylon-6	Dark red	6	3
		Wool	Red	6	3
	Acid	Nylon-6	Dark red	6	3
		Wool	Red	6	3
	Basic	Acrylic	Orange–red	6	2

[a] Fastness grades used in the table: 1, poor; 2, moderate; 3, fairly good; 4, good; 5, very good; 6, excellent.

3.3 Dyeing methods

All dyeings were carried out on piece using cotton, viscose rayon, satin, wool, nylon-6 and acrylic, using the following procedures.

3.3.1 As direct dyes

The fabric was immersed in a dyebath set at 50°C containing dyestuff solution, 15% sodium sulphate and 1% sodium carbonate; the bath was then heated to boiling point for 15 min and further sodium sulphate was then added and dyeing continued for 30 min. The dyed fabric was then washed with water and dried.

3.3.2 The acid dyes

The fabric was immersed in a cold dyebath containing the dyestuff solution, 10% sodium sulphate and 3–5% acetic acid (30% by vol.). The bath was heated to boiling over 15 min, maintained at the boil for a further 30 min and then washed with water and dried.

3.3.3 As basic dyes

The fabric was immersed in a dyebath (set at 70°C) containing the dye solution, 4% acetic acid (50% by vol.), 10% sodium acetate, and 20% sodium sulphate. The bath was then heated to boiling over 45 min, and boiled for a further 45 min. The fabric was finally washed with water and dried.

3.4 Fastness properties of the dyed samples

SDC standard methods[10] were used to evaluate the fastness properties (to daylight and to washing) of the dyed samples. Relevant data are given in Table 4.

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