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Activated Thiocyanates in the Synthesis of Heterocyclic Hansa Yellow Analogues. Synthesis and Colour Measurements of 1-(5'-Imino-4'-phenyl-4',5'-dihydro-1',3',4'-thiadiazol-2'-yl)-3-(pyrid-2'-yl)amino-1,2,3-trioxopropane 2-arylhydrazone Derivatives as Dyes for Synthetic-Polymer Fibres

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ABSTRACT

In a sequence of reactions the activated thiocyanate derivative 2 was used to synthesize new Hansa Yellow dyestuffs embodying two heterocyclic moieties. The structure of the dyes was inferred from spectral and analytical data. Spectral behaviour of the dyes indicated that they existed essentially in the hydrazone form (5-C).

Dyeings of the compounds on polyester were assessed with a view to evaluating the percentage reflectance of the dyed fibre at different wavelengths in the visble region and the Kubelka–Munk equation was used to calculate the K/S function of the dyed materials.

1 INTRODUCTION

Since Victor Meyer's[1] first report on the coupling of diazonium salts with activated carbon compounds, and until recently, the primary importance of acetoacetarylamide coupling components was in the field of Hansa Yellow dyes and pigments.[2–4]

Although the traditional carbocyclic derivatives of these dyes still dominate, the development of new heterocyclic Hansa Yellow analogues affords new[5–8] Hansa Yellows with a fairly full range of hues being

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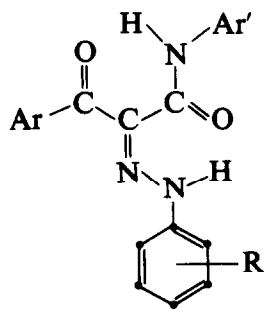
especially well represented among yellows, oranges and reds. They have very good high all-round fastness properties, in particular towards light, heat, water, acids and alkalis.

The presence of such heterocyclic moieties in the structure of these Hansa Yellow analogues generally improve[7,8] the dyeing behaviour of these dyes towards acetate and/or other synthetic fibres.

Although several studies in the literature include variations of the R-, Ar- and Ar'-moieties of the dye



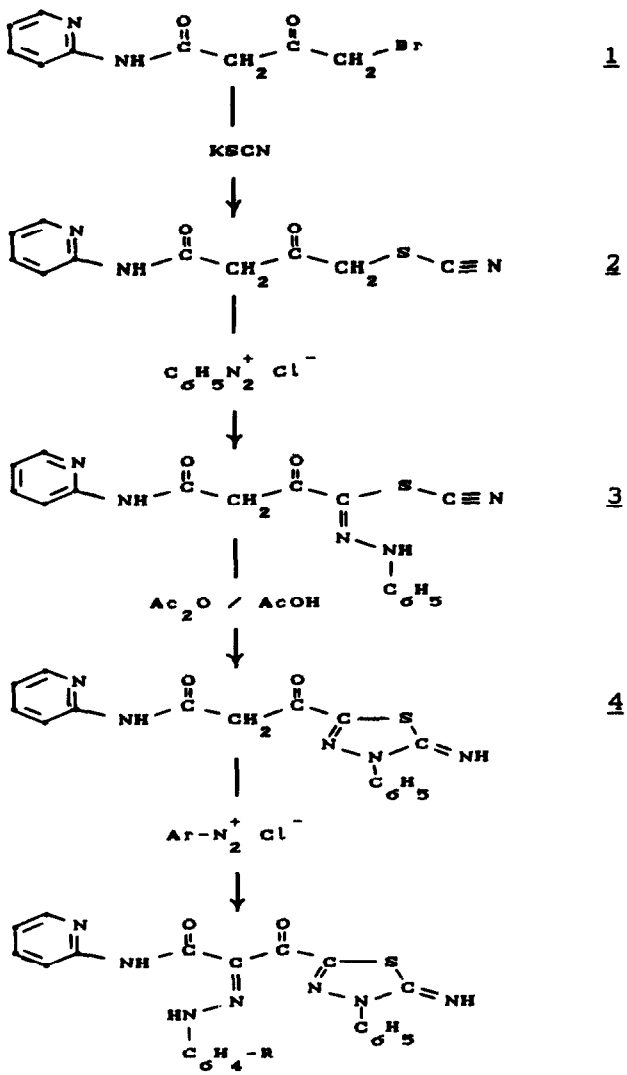
(A)

molecule (A), a survey of the literature suggested further areas for the synthesis of new heterocyclic Hansa Yellow analogues embodying two heterocyclic moieties in their structure. Thus, as an extension of a program dealing with the synthesis and chemical reactivity of heterocyclic Hansa Yellow dyes and pigments,[5,6,9] this present communication presents a new route for the synthesis of 1-(5'-imino-4'-phenyl-4',5'-dihydro-1',3',4'-thiadiazol-2'-yl)-3-(pyrid-2'-yl)aminopropane 1,3-dione and its use in the preparation of new heterocyclic Hansa Yellow dyes for synthetic-polymer fibres.

2 RESULTS AND DISCUSSION

The general sequence for the preparation of the dyes is outlined in Scheme 1.

Refluxing an ethanolic solution of 4-bromo-3-oxo-*N*-(pyrid-2-yl)butanamide (**1**)[5] with potassium thiocyanate afforded the corresponding activated thiocyanate derivative (**2**) in almost quantitative yield. In addition to bands corresponding to ketonic and amide moieties, the IR spectra of the product had an absorption at 2350 cm^{-1} which can be attributed to the stretching vibration of the —SCN group. The product reacts with



Scheme 1.

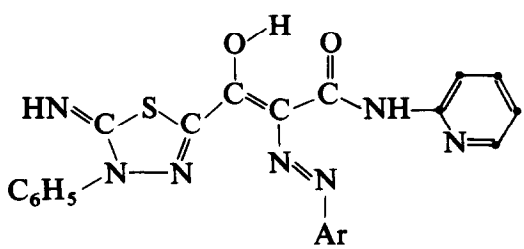
diazotized aniline in ethanolic solution containing sodium acetate to yield 3,4-dioxo-*N*-(pyrid-2'-yl)-4-thiocyanobutanamide 4-phenylhydrazone (**3**) as the sole product. The structural assignment of this compound was based on elemental and spectral analyses. In addition to absorption bands for hydrogen-bonded NH groups (amide and hydrazone moieties) near 3400 cm^{-1} and thiocyano groups at 2300 cm^{-1}, the IR spectrum

showed two carbonyl absorptions near 1665 and 1690 cm^{-1}, assigned to the thiocyano-acetyl and amide moieties respectively. The ^1H NMR spectrum of this phenylhydrazono-thiocyano dye exhibited a singlet, corresponding to the methylene-protons at δ 4·49 ppm.

When refluxed in acetic acid/acetic anhydride, **3** gave 1-(5'-imino-4'-phenyl-4',5'-dihydro-1',3',4'-thiadiazol-2'-yl)-3-(pyrid-2'-yl)aminopropane 1,3-dione (**4**) in good yield. The IR spectrum of this revealed absorption bands at 3432, 1708, 1628, 1596 and 1576 cm^{-1}, which can be attributed to stretching vibrations of NH, amidic and ketonic CO, exo and endo C=N groups respectively.

The synthetic potentiality of the thiadiazolyl derivative **4** was explored via its use as an intermediate for the synthesis of the projected dyes. Thus, treatment with cold solutions of arene-diazonium salts in an ethanol-buffered solution afforded the corresponding heterocyclic Hansa Yellow dyes, namely, 1-(5'-imino-4'-phenyl-4',5'-dihydro-1',3',4'-thiadiazol-2'-yl)-3-(pyrid-2'-yl)amino-1,2,3-trioxopropane 2-arylhydrazone derivatives (**5a–g**).

The IR spectra of these new Hansa Yellow analogues were characterized by absorption bands in the region of 1670–1620 cm^{-1}, which could be assigned to stretching vibrations of carbonyl groups. The higher frequency band (1670 cm^{-1}) is due to the amide I band, while the other band (1620 cm^{-1}) corresponds to the thiadiazoloyl-carbonyl stretching vibration. The appearance of the latter band excludes the possibility of these dyes existing as hydroxy-azo configuration (**5-A**).

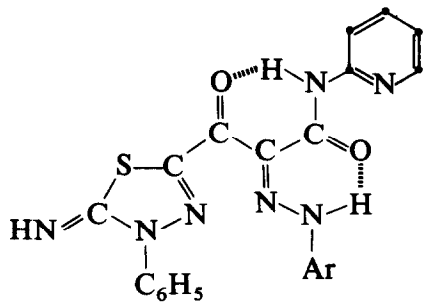


(5-A)

The spectral data show that the thiadiazoloyl carbonyl bands of these hydrazono derivatives (**5a–g**) were at markedly lower frequency than those of the corresponding β-ketopyridide (**4**).

Among the structural factors leading to a lowering of the stretching vibration of carbonyl groups are conjugation and hydrogen bonding. However, even if allowance is made for conjugation, the CO frequencies of the dyes under consideration are still much lower than those encountered in other α, β- unsaturated ketones. This significant difference suggests that the thiadiazoloyl CO group of these dyes is involved in

a stable hydrogen-bonded ring structure, as shown in the proposed structure (**5-B**).



(5-B)

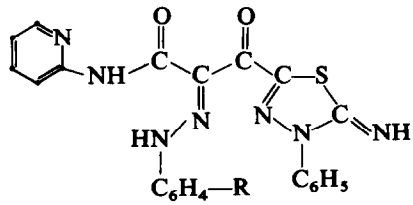
TABLE 1
Characterization Data for Compounds **2–4** and **5a–g**

No.	*M.P.* (°C)	*Formula* (*M. wt*)	*Analyses Calcd/Found*			*UV spectra*[a]	
			%C	*%H*	*%N*	λ_{max}[b] (*nm*)	*log ε*
2	310–311	$C_{10}H_9N_3SO_2$ (235·25)	51·05 50·83	3·86 3·94	17·86 17·67	—	—
3	108–109	$C_{16}H_{13}N_5SO_2$ (339·36)	56·62 56·90	3·86 3·78	20·64 20·41	—	—
4	122–123	$C_{16}H_{13}N_5SO_2$ (339·36)	56·62 56·38	3·86 3·84	20·64 20·77	—	—
5a	162–164	$C_{25}H_{21}N_7SO_4$ (515·53)	58·24 58·41	4·11 4·06	19·02 19·40	412	4·01
5b	177–178	$C_{23}H_{19}N_7SO_3$ (473·49)	58·34 58·52	4·04 4·17	20·71 20·46	432	4·14
5c	150–153	$C_{22}H_{17}N_7SO_2$ (443·47)	59·58 59·29	3·86 3·97	22·11 21·88	400	4·20
5d	185–187	$C_{22}H_{16}F_7SO_2$ (461·47)	57·26 56·97	3·50 3·58	21·25 21·40	421	4·03
5e	230–231	$C_{24}H_{21}N_7SO_3$ (487·53)	59·12 59·19	4·34 4·21	20·11 19·95	426	4·04
5f	210–213	$C_{23}H_{19}N_7SO_2$ (457·49)	60·38 60·09	4·19 4·22	21·43 21·73	429	4·09
5g	195–197	$C_{25}H_{16}N_8SO_2$ (468·48)	58·96 59·12	3·44 3·49	23·92 23·56	406	4·05

[a] Spectral parameters of (LWB) of Hansa Yellow analogues (**5a–g**) in ethanol.
[b] λ_{max} for (LWB).

TABLE 2

Percentage Reflectance (*R*), Kubelka–Munk Function (*K/S*) and Colour Shades of Terylene Dyed with the Hansa Yellow Analogues **5a–g**



Dye No.	*R*	*Colour of crystals*	*%R*[a]	*K/S*	*Shade on terylene*
5a	*p*-COOEt	Pale yellow	02·87	16·4176	Lemon yellow
5b	*p*-OMe	Orange	02·60	18·2451	Canary yellow
5c	—H	Yellowish orange	02·81	16·7853	Yellowish orange
5d	*p*-F	Yellowish	10·88	03·6520	Lemon yellow
5e	*p*-OEt	Yellow	06·30	06·9890	Yellow
5f	*p*-Me	Brownish red	13·46	02·7833	Light pink
5g	*p*-CN	Reddish brown	28·02	00·9247	Beige tint

[a] Measured at 400·0 nm.

Hence, conjugation of the thiadiazolyl-carbonyl group and possible intramolecular hydrogen bonding in these Hansa Yellows probably result in the shift of the CO frequencies to lower wavenumber. This shift, in some cases, such as in dye **5d**, is apparently so large that this carbonyl band cannot be resolved from the aromatic C=C band near 1600 cm^{-1}.

Evidence for the presence of these diazonium coupling products, apparently exclusively in the hydrazone form, is apparent from electronic spectral data, where most of these Hansa Yellow analogues show three main absorption bands in the 432–245 nm region. Spectral parameters of the longest wavelength band (LWB) are given in Table 1.

The UV spectra of monophenylazo compounds differ from those of monophenyl hydrazones.[10] The azo compounds have a strong conjugation-band in the region 270–280 nm. The monophenylhydrazones give a weak absorption band (or no band) at 248–295 and a strong band at wavelengths higher than 320 nm. Further, the UV spectra of arylhydrazones derived from the reaction of quinones with *N*-alkylarylhydrazines, unlike those of the ortho and para hydroxyazo compounds which can tautomerize into the corresponding arylhydrazones, are largely independent of the polarity of the solvent.[11] Electronic absorption spectra of dyes (**5a–g**) are similar to those of typical hydrazones. The relatively small differences observed are caused by solute–solvent interactions.[12]

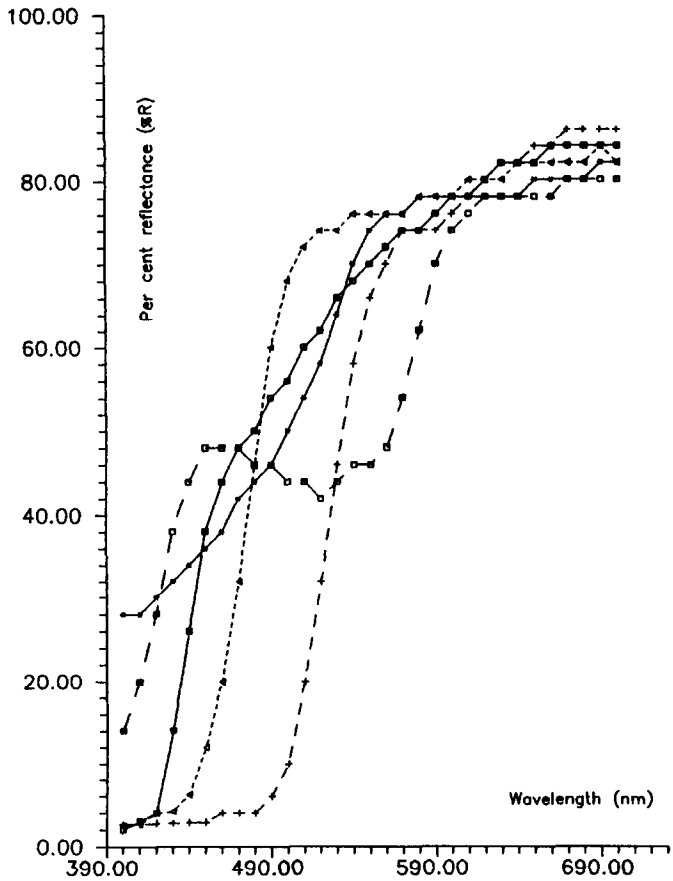


Fig. 1. Plot of change in per cent reflectance (R) with change in wavelength (λ) in the visible region for a terylene fibre dyed with different heterocyclic Hansa Yellow analogues (**5a–g**): **5a** (-□-□-□-), **5b** (-Δ- -Δ- -Δ-), **5c** (-×-×-×-), **5f** (□-□-□) and **5g** (-•-•-•-).

While the ^{1}H NMR spectrum of dye **5a** exhibits characteristic signals for aromatic, imino, amido, hydrazono and carbethoxy protons (See Experimental), EIMS of another member of this series of dyes, namely **5g**, revealed the absence of the molecular ion peak, but the presence of a base peak at 93 mass units. Such spectral results support the structure of these dyes, and consequently establish the proposed structure for the Hansa Yellows prepared in this investigation.

The dyeing performance of the new Hansa Yellow analogues (**5a–g**) on poiyester was assessed with a view to evaluate the effect of changing the nature of the substituents in the arylhydrazone moiety on the colour strength on the dyed fibre.

While Table 2 depicts *K/S* values and colour hues of the polyester

fibre, Figure 1 shows illustrative examples for the change in percentage reflectance (%R) with changing wavelength (λ) for the fabric after being dyed with these Hansa Yellows.

From the results, it is clear that most of the new Hansa Yellow dyes showed good affinity towards polyester. The deep shades of the dyes may be attributed to the absence of solubilizing sulphonic or carboxylic acid groups.

Evaluation of tristimulus values (x, y, z) for different synthetic fabrics, together with colour difference between the dyed samples using FMC-II units are under investigation and will be reported later.

3 EXPERIMENTAL

All melting points are uncorrected. IR spectra (KBr) were recorded on an SP 2000 Pye-Unicam spectrometer. ^{1}H-NMR spectra ($CDCl_3$) were determined on a Varian EM 360 spectrophotometer at 80 MHz using TMS as internal standard. EIMS were carried out on a Varian 111 spectrometer operating at 70 eV. UV and visible measurements were made from ethanolic solutions on a Pye-Unicam SP 500 spectrophotometer. Physical data for the prepared compounds are listed in Table 1. (Textile dyeing and colour measurements were carried out at the El-Nasr Company, El-Mehalla, Egypt.)

3.1 Preparation of 4-bromo-3-oxo-N-(pyrid-2'-yl)butanamide (1)

This was obtained as yellow crystals, m.p. 174–175°C (ethanol) through bromination of the corresponding 2-pyridide derivative, according to the previously reported method.[5]

3.2 Preparation of 3-oxo-*N*-(pyrid-2'-yl)-4-thiocyanobutanamide (2)

Equimolar amounts (0·005 mol) of **1** and potassium thiocyanate were heated at 80°C in a 70% ethanol–water mixture (25 ml) for 2 h and then cooled. Extraction of the reaction mixture with chloroform followed by separation, drying and evaporation (under reduced pressure) of solvent from the organic layer afforded the product, which was recrystallized from ethanol as greenish yellow crystals in 82% yield. IR (cm^{-1}): 3500–3350 (amide NH), 2350 (SCN group), 1720 and 1690 (ketonic and amidic carbonyls).

3.3 Preparation of 3,4-dioxo-*N*-(pyrid-2'-yl)-4-thiocyanobutanamide 4-phenylhydrazone (3)

An ice cold solution of benzenediazonium chloride, prepared from aniline (4·65 g, 0·05 mol) and the appropriate amount of sodium nitrite (3·45 g, 0·05 mol) and hydrochloric acid (13 ml), was added to a well-stirred and cold solution of the thiocyano-butanamide derivative **2** (11·8 g, 0·05 mol) in ethanol (100 ml) containing sodium acetate trihydrate (4 g). The solid product so formed was collected by filtration and recrystallized from ethanol to give **3** as reddish brown crystals in good yield. IR (cm^{-1}): 3400–3350 (NH of amide and hydrazone moieties), 2300 (SCN), 1690 and 1665 (amidic and thiocyano-acetyl moieties respectively). ^1H NMR spectrum (δ/ppm): 12·15 (s, 1H, hydrazone N<u>H</u>), 8·11–7·27 (m, 9H, aromatic and 1H, N<u>H</u> of amide moiety) and 4·49 (s, 2H, C<u>H</u>$_2$).

3.4 Cyclization of 3. Formation of 1-(5'-imino-4'-phenyl-4',5'-dihydro-1',3',4'-thiadiazol-2'-yl)-3-(pyrid-2'-yl)aminopropane 1,3-dione (4)

A mixture of **3** (3·4 g, 0·01 mol), acetic acid (20 ml) and acetic anhydride (20 ml) was heated at reflux for 5 h, left to cool and poured on cold water (60 ml). The precipitated product was filtered, dried and recrystallized from benzene to give **4** as brown-coloured crystals. IR (cm^{-1}): 3432, 1708, 1628, 1596 and 1576, corresponding to imino & amide NH, amidic and thiadiazoloyl CO, exo and endo C=N groups respectively.

3.5 Preparation of 1-(5'-imino-4'-phenyl-4',5'-dihydro-1',3'.4'-thiadiazol-2'-yl)-3-(pyrid-2-yl)amino-1,2,3-trioxopropane 2-arylhydrazono Hansa Yellow dyestuffs (5a–g)

A well-stirred solution of the aromatic amine (0·01 mol) in 2 N hydrochloric acid (60 ml) was cooled in an ice-salt bath and diazotized with 1 N sodium nitrite solution (50 ml). This solution was added slowly with stirring and cooling to the thiadiazolyl-aminopropane derivative **4** (3·4 g, 0·01 mol) in ethanol (60 ml) buffered with hydrated sodium acetate (1 g in 10 ml water). When coupling was complete, the mixture was stirred for a further 30 min. The precipitate was filtered, washed with water, dried and recrystallized from ethanol or acetic acid to give the required dyes (as yellow to brownish coloured crystals) in 64–71% yield. ^1H NMR spectrum of **5a** (δ/ppm): 12·27 (s, 1H, N<u>H</u> of hydrazone moiety), 9·06 (s, 1H, amide N<u>H</u>), 7·71–6·64 (m, 13H, aromatic protons), 4·30 (q, 2H, —C<u>H</u>$_2$CH$_3$), 3·58 (s, 1H, imino N<u>H</u>) and 2·03 (t, 3H, —CH$_2$C<u>H</u>$_3$). EIMS of **5g** (m/z, relative abundance %): 135 (38·01), 93 (100), 91 (21·40) and 77 (33·06).

3.6 Dyeing of polyester fibre

The dye-bath (liquor ratio, 1:40) containing 1% dye, 2 g/litre Dekol-N (BASF) dispersing agent and 5 g/litre Levagol PT (methyl salicylate carrier, Bayer) was brought to 60°C. The material was entered at 60°C and the temperature was raised gradually to boiling over 45 min. Dyeing was continued at the boil for about 2 h. The dyed material was rinsed and then soaped with a non-ionic detergent.

3.7 Colour measurements

All the dyed samples were tested and evaluated for their colour fastness. The percentage reflectance (%R) of the dyed material was measured at different wavelengths in the visible region (400–700 nm) using an ACS-600 colour control system. The Kubelka–Munk equation was applied to calculate the function *K/S* for the fibre after being dyed with the prepared Hansa Yellows.

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