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Some Monoazoacetoacetanilide Pigments Derived from Heterocyclic Diazo Components

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ABSTRACT

In the case of azo disperse dyes, the replacement of traditional carbocyclic diazo components with heterocyclic derivatives generally leads to a bathochromic shift of the absorption band and an increase in molar extinction coefficient, features which have been exploited commercially. PPP molecular orbital calculations suggested that a similar, though less pronounced, effect might be expected with monoazoacetanilide pigments (Hansa Yellows). A series of monoazoacetoacetanilides derived from heterocyclic diazo components was prepared using a non-aqueous azo coupling method. The products showed interesting colouristic properties and enhanced solvent fastness compared with the classic Hansa Yellows, but inferior fastness to light and heat.

1 INTRODUCTION

It has been known for some time that with many azo dyes the replacement of traditional carbocyclic diazo components with heterocyclic diazo components can lead to a pronounced bathochromic shift of the visible absorption band and an increase in molar extinction coefficient.[1-3] This has led to commercial exploitation, particularly in the area of disperse dyes for polyester, with the introduction of a number of high tinctorial strength red and blue dyes derived mainly from 2-aminothiazoles, 2-aminobenzothiazoles and 2-aminothiophens as diazo components and *N*,*N*,-dialkylanilines as coupling components.[2,3] In the range of classic organic pigments

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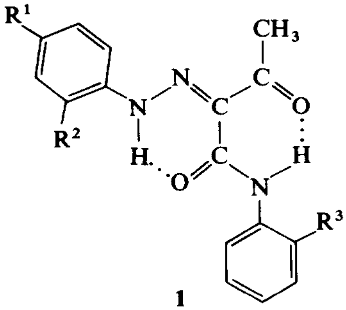
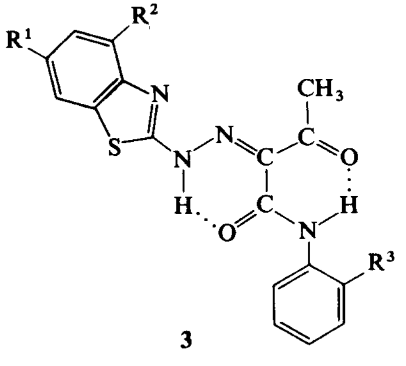
for printing ink, paint and plastic applications, by far the most important yellow products are azo pigments derived from acetoacetanilide coupling components.[4] In the case of these azoacetoacetanilide pigments, it was of interest to investigate whether the use of heterocyclic diazo components might, in a similar way, lead to an extension of the shade range of the commercial products, which is currently restricted to yellows and oranges, and, arguably of greater commercial significance, to produce products of superior tinctorial strength. In this paper, the preparation of a series of azoacetoacetanilide pigments derived from heterocyclic diazo components is reported. The series comprises the thiazole derivative (**2**), the benzothiazole derivatives (**3a–d**) and the thiophen derivative (**4**); the pigments are compared in terms of their structural, colouristic and, where appropriate, application properties with three, representative carbocyclic monoazoaceto-



1

	R¹	R²	R³
1a	H	H	H
1b	CH_3	NO_2	H
1c	NO_2	CH_3O	CH_3O

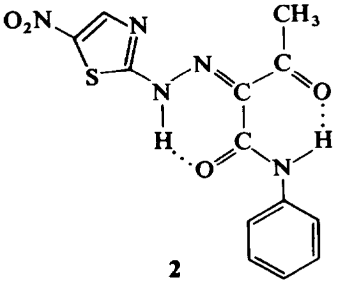
Scheme 1



3

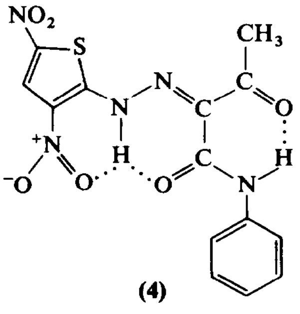
	R¹	R²	R³
3a	OCH_3	H	H
3b	NO_2	H	H
3c	NO_2	CH_3O	H
3d	NO_2	CH_3O	CH_3O

Scheme 3



2

Scheme 2



(4)

Scheme 4

acetanilides, the parent compound (**1a**) and two important commercial products, CI Pigment Yellow 1 (**1b**) and CI Pigment Yellow 74 (**1c**) (Schemes 1–4).

2 RESULTS AND DISCUSSION

2.1 Synthesis

Classic azoacetoacetanilide pigments are prepared by an aqueous diazotisation and coupling procedure, which leads directly to a pure product in high yield and in a physical form suitable for application. However, attempts to prepare compounds **2**, **3a–d** and **4** using this standard method either failed completely or gave a low yield of a highly impure product, probably due to the instability of the heterocyclic diazonium salts in water at a pH sufficiently high to allow coupling to take place. It has been reported that diazotised aminobenzothiazoles couple successfully with a range of reactive methylene coupling components in organic solvents in the presence of sodium acetate.[5] In the present study, it was found that reasonable yields of the heterocyclic pigments could be obtained (Table 1) when the coupling was carried out in acetic acid.

2.2 Structure of the pigments

It has been demonstrated conclusively from a series of investigations using a variety of techniques that azoacetoacetanilides exist exclusively as ketohydrazones both in solution and in the solid state.[6–13] For example, the solid state IR spectra of the pigments show a single carbonyl absorption in

TABLE 1
Yields and Analytical Data

Compound	*Yield* (%)	*Molecular formula*	*Analysis*					
			Calculated (%)			*Experimental* (%)		
			C	*H*	*N*	*C*	*H*	*N*
2	42	$C_{13}H_{11}N_5O_4S$	46·8	3·3	21·0	46·8	3·2	20·9
3a	69	$C_{17}H_{13}N_5O_4S$	53·2	3·4	18·3	53·1	3·3	18·2
3b	52	$C_{18}H_{16}N_4O_3S$	58·7	4·4	15·2	58·4	4·2	15·0
3c	45	$C_{18}H_{15}N_5O_5S$	52·3	3·7	16·9	51·9	3·3	17·1
3d	53	$C_{19}H_{17}N_5O_6S$	51·4	3·9	15·8	51·4	3·7	15·8
4	45	$C_{13}H_{11}N_5O_4S$	44·5	2·9	18·6	44·4	3·0	18·7

TABLE 2
IR Spectral Data and Melting Points

Compound	*C=O stretching frequency (cm^{-1})*	*Melting point (°C)*
2	1 678	250
3a	1 676	197
3b	1 667	263
3c	1 675	243
3d	1 675	278
4	1 676	276[a]

[a] With strong exothermic decomposition.

the range 1658–1690 cm^{-1} consistent with a ketohydrazone form with extensive intramolecular hydrogen bonding,[6–9] and this has been confirmed in a number of cases by X-ray crystallography.[10–12]

The heterocyclic pigments (**2**–**4**) gave similar IR spectra to the carbocyclic derivatives, showing in each case a carbonyl absorption (Table 2) consistent with their existence as ketohydrazones. The extreme insolubility of the pigments precluded a detailed investigation by NMR spectroscopy. However, ^{1}H and ^{13}C spectra were obtained for compound **2**, the most soluble derivative in the series, in d^5-nitrobenzene at 80°C. The ^{13}C-NMR spectrum was found to be very similar to that of the parent monoazoacetoacetanilide (**1a**). For example, the methyl, amide, C=N and ketone signals appeared at δ 25·8, 199·5, 131·8 and 161·2, respectively, compared with the signals at δ 25·9, 198·5, 126·0 and 166·6 for compound **1a**. The ^{1}H-NMR spectrum of compound **2**, also, was similar to that of compound **1a**, with the amide and hydrazide protons appearing characteristically at δ 11·1 and 14·8, respectively, compared with δ 11·5 and 14·7 for compound **1a**. These data confirm that compound **2** exists in solution as a ketohydrazone. An interesting observation was that the ^{1}H-NMR spectrum of this pigment showed two sets of signals of similar intensity in close proximity. This is probably due to the existence of two geometrical configurations, the Z- and E-configurations, in roughly equal proportions. Jirman and Lycka report NMR evidence for the existence of Z- and E-configurations of a number of related carbocyclic derivatives, although in those cases the Z-configuration greatly predominates.[13]

2.3 Colour and constitution relationships

The use of the PPP molecular orbital (MO) method to account for the UV/visible spectra of organic colorants is now well established.[14,15] In

TABLE 3
Comparison between Calculated and Experimental UV/Visible Spectral Data for Some Monoazoacetoacetanilides

Compound	*Calculated values (PPP–MO method)*		*Experimental values (1,3,4-trichlorobenzene)*	
	λ_{max} (*nm*)	f_{osc}	λ_{max} (*nm*)	$\varepsilon \times 10^{-4}$ ($1\,mol^{-1}\,cm^{-1}$)
1a	376	1·24	381	2·70
1b	442	0·61	417	1·96
1c	420	1·34	423	3·71
2	477	1·42	412	2·58
3a	477	1·57	410	2·25
3b	460	1·66	395	3·68
3c	482	1·54	410	3·49
3d	484	1·55	414	3·42
4	494	1·08	435	2·89
	422	0·39	377	1·30

particular, an approach using a generalised set of parameters has proved very successful in predicting λ_{max} values, while the calculated oscillator strength values may be used to predict molar extinction coefficients. In an investigation of colour and constitution relationships in monoazoacetoacetanilide pigments (Hansa Yellows), the correlation between the results of optimised PPP–MO calculations and data obtained from the UV/visible spectra of a range of the pigments has been reported.[6] It was found that the λ_{max} values of the pigments for solutions in DMF could be predicted with a reasonable degree of accuracy, and also that there was a reasonable qualitative correlation between the experimental molar extinction coefficients and the calculated oscillator strengths. Subsequently, it has been demonstrated that the PPP–MO calculations using the same set of optimised parameters could be applied successfully to account for the colouristic properties of a range of diazoacetoacetanilides (Diarylide Yellows).[7] Similarly, Hallas and Marsden have reported a good correlation between results of PPP–MO calculations and spectral data for a series of *N*-phenylpyrrolidinylazo disperse dyes derived from a variety of carbocyclic and heterocyclic diazo components.[16] The results of PPP–MO calculations carried out on compounds **1**–**4** are given in Table 3. The parameters for the heteroatoms were those adopted by Hallas and Marsden for their series of azo disperse dyes, while the remainder of the parameters were those optimised previously for the carbocyclic azoacetanilides. In a previous study,[6,7] DMF was used as the common solvent for recording the UV/visible spectra of the

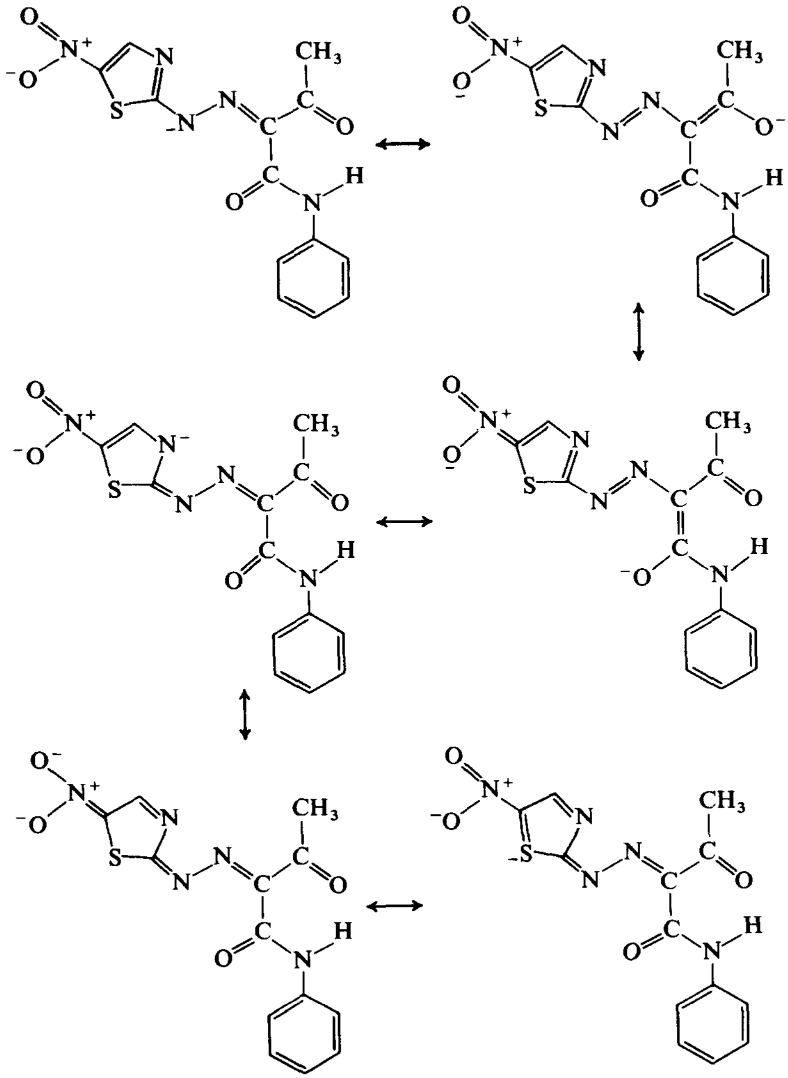


Fig. 1. Resonance-stabilised anion (incorporating the possibility of valence-shell expansion at sulphur) from deprotonation of **2**.

pigments. However, this solvent proved unsuitable for the heterocyclic derivatives as it led to an additional absorption band at higher wavelength, which is probably due to the deprotonated species. The relative ease of formation of the anions from these pigments may be attributed to the extensive resonance stabilisation, for example as shown for compound **2** in Fig. 1. The spectral data obtained for the series of compounds in the less basic solvent, 1,2,4-trichlorobenzene, are also given in Table 3. It can be seen that the λ_{max} values calculated for the heterocyclic pigments (**2**–**4**) are around

60–70 nm bathochromic compared with the experimental values, although, interestingly, the trends in the values are in reasonable qualitative agreement. It is also of interest that the benzothiazole pigments (**3b–d**) show high molar extinction coefficients, comparable with that of CI Pigment Yellow 74 (**1c**), a high strength monoazoacetoacetanilide, although they do not offer the colour strength advantage over this compound suggested by the calculated oscillator strength values. The thiophen derivative (**4**) is of some interest colouristically in that it is significantly more bathochromic than the other members of the series, is orange in the solid state and has a reasonably high extinction coefficient. Overall, although there is some qualitative correlation between calculated and experimental spectral data for the heterocyclic pigments, the quantitative agreement is less good. This may well be associated with the combined use of two sets of parameters empirically optimised for different series of compounds. No attempt was made to optimise the calculations further by producing a more mutually compatible set of parameters.

2.4 Application properties

In their purified forms after recrystallisation, each of the heterocyclic azo pigments exhibited a bright yellow or, in the case of compound **4**, orange colour. However, only compounds **2**, **3b** and **4** were obtained directly from the coupling reaction in sufficient purity to warrant investigation of the application properties. For the purposes of evaluation of the properties of the pigments, an industrial paint formulation based on an alkyd/melamine-formaldehyde (MF) resin system requiring drying by stoving at 140°C was chosen. Such an application is fairly demanding, particularly with respect to fastness to light, solvents and heat. The results of the evaluation are contained in Table 4. The commercial Hansa Yellows (**1b** and **c**) exhibit

TABLE 4
Pigment Properties in Industrial Paint Application

Compound	*Overpaint fastness*	*Heat stability*	*Light-fastness*		
			Full strength paint	*1:1 reduction with TiO_2*	*1:3 reduction with TiO_2*
1b	1–2	5	7	7	6–7
1c	2	5	7	7	6–7
2	2–3	5	5	4	2
3b	2–3	5	5–6	4–5	4
4	2	1–2	4–5	4	2

excellent light-fastness and stability of colour at 140°C (section 4·5). However, they show poor resistance to solvents, assessed as overpaint fastness (section 4·5), accounting for their limited application in industrial paints. The heterocyclic derivatives (**2**, **3b** and **4**) show marginally better overpaint fastness, presumably due to reduced solubility as a result of an increase in molecular size. However, the pigments show significantly inferior light-fastness compared with the commercial products. The poor light-fastness of the dinitrothiophen derivative (**4**) was especially disappointing, in view of its interesting colouristic properties and the general observation that a nitro group *ortho* to the hydrazone function can confer improved photostability as a result of intramolecular hydrogen bonding.[6] The poor thermal stability of compound **4** compared with the other pigments investigated was consistent with the results obtained using differential scanning calorimetry (DSC), which demonstrated that, while the others exhibited normal melting points, the melting of compound **4** was accompanied by a strong exothermic decomposition (Table 3).

3 CONCLUSION

Monoazoacetoacetanilide pigments may be prepared from a range of heterocyclic diazo components using a non-aqueous azo coupling technique. PPP–MO calculations provide a reasonable qualitative account of the UV/visible spectral data for the pigments. In an industrial paint application, certain of the pigments exhibited interesting colouristic properties and superior solvent resistance compared with the classic Hansa Yellows, but inferior light-fastness and thermal stability.

4 EXPERIMENTAL

4.1 Instrumental methods

IR spectra were recorded as KBr discs with a Perkin-Elmer 1740 Fourier Transform spectrometer. Melting points are extrapolated onset temperatures obtained using a Mettler DSC30 differential scanning calorimeter with a heating rate of 5 K min^{-1} and a flowing nitrogen atmosphere. UV/visible spectra were recorded on a Perkin-Elmer Lamda 2 spectrophotometer. ^{1}H NMR spectra were recorded on a Perkin-Elmer R32 spectrometer and ^{13}C NMR spectra using a Brooker WP200SY instrument. C, H and N analyses were carried out in the Department of Applied Chemical Sciences, Napier Polytechnic, Edinburgh, UK.

4.2 PPP–MO calculations

A standard PPP–MO procedure was used within the fixed β approximation.[15] Two-centre repulsion integrals were determined using the Nishimoto–Mataga relationship,[17] and electronic excitation energies were refined by a limited configuration interaction treatment involving nine singly excited configurations obtained by promoting an electron from the three, highest, occupied molecular orbitals to the three, lowest, unoccupied molecular orbitals.

4.3 Heterocyclic amines

The aminobenzothiazoles were prepared by established literature procedures.[18] The authors are grateful to Yorkshire Chemicals (Leeds, UK) for a sample of 2-amino-5-nitrothiazole and to ICI Colours & Fine Chemicals (Blackley, Manchester, UK) for a sample of 2-amino-3,5-dinitrothiophen.

4.4 Synthesis of the pigments

Compounds **2**–**4** were prepared by the following procedure. The appropriate amine (0·025 mol) was diazotised according to literature procedures.[18–20] The diazonium salt solution was added with stirring over 5 min to a solution of the acetoacetanilide coupling component (0·025 mol) in acetic acid (300 cm^3) cooled to 15°C. Anhydrous sodium acetate was added in portions until coupling became apparent, and the reaction mixture was then stirred at 15°C for 1 h. Water (300 cm^3) was added, the mixture heated to 95°C, filtered, the product washed with water until salt free and dried at 60°C. Analytically pure samples were obtained by multiple recrystallisation from acetic acid. The following NMR data were obtained for compound **2** in d^5-nitrobenzene at 80°C: δ_H (in each case a closely spaced set of double signals of roughly equal intensity was observed) 2·55 (3H, s, CH_3), 7·19, 7·37, 7·63 (5H, multiplets, phenyl-H), 8·23 (1H, s, thiazole-H), 11·06 (1H, br s, amide NH), 14·84 (1H, br s, hydrazone NH); δ_C 25·8 (CH_3), 131·8 (C=N), 166·6 (amide C=O), 199·5 (ketone C=O), aromatic signals largely obscured by signals due to residual solvent.

4.5 Preparation of industrial stoving paints and assessment of pigment properties

Alkyd/MF-resin-based full-strength paints and white reductions were prepared, and assessments of fastness to light, heat (to 140°C) and overpaint were carried out according to previously reported procedures.[21]

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