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Colour and Constitution Relationships in Organic Pigments. Part 2—Disazoacetoacetanilides*

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ABSTRACT

Disazoacetoacetanilides provide the most important classical organic pigments in the yellow shade area, especially for printing ink applications. As a first step in attempting to establish the colour and constitution relationships in this series of products, a number of disazo pigments were synthesised and their UV/visible spectral behaviour in solution investigated. PPP molecular orbital calculations, using a generalised set of parameters optimised previously for a series of monoazoacetoacetanilides and assuming that the compounds exist exclusively in bisketohydrazone tautomeric forms with planar molecular geometry, provided a good correlation between calculated and experimental λ_{max} *values for the principal absorption band, and in addition there was a reasonable qualitative agreement between molar extinction coefficients and the calculated oscillator strengths. The spectroscopic evidence for the bisketohydrazone form is discussed. The effect of rotation about the biphenyl link in C.I. Pigment Yellow 12 on the predicted spectroscopic properties was investigated using an empirical correction to the calculations.*

1 INTRODUCTION

The industrial production of organic yellow pigments is dominated by a range of disazoacetoacetanilides commonly referred to as Diarylide Yellows.[1,2] Of particular commercial significance are the Benzidine Yellows, most notably C.I. Pigments Yellow 12, 13 and 14, derived from reaction of

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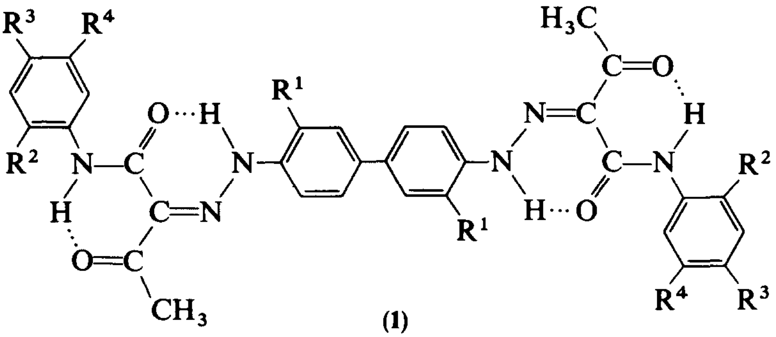
tetrazotised benzidine derivatives with acetoacetanilide coupling components. These pigments are related structurally to the monoazoacetoacetanilides (Hansa Yellows) but exhibit considerably superior tinctorial strength and transparency and find their principal application in printing inks where these optical properties together with the relatively low cost of the products are of prime importance. In addition, because of their larger molecular size, these disazo pigments show enhanced fastness to solvents and to heat compared with the corresponding monoazo pigments and consequently they are suitable for use to a certain extent in the colouration of plastics and elastomers. The principal deficiency of the Benzidine Yellows is their lightfastness, which is inadequate in most cases for paint applications, especially where exterior use is envisaged. However, the incorporation of an appropriate substituent pattern into the coupling component ring can lead to enhanced lightfastness, as for example in the reddish-yellow C.I. Pigment Yellow 83, derived from 4-chloro-2,5-dimethoxyacetoacetanilide, which is suitable for use in a range of more demanding applications. Disazoacetoacetanilides of other structural types, such as the greenish-yellow C.I. Pigment Yellow 16 derived from a bisacetoacetanilide coupling component, are produced but are considerably less significant commercially than the Benzidine Yellows.

As with the corresponding monoazo pigments, the colour of disazoacetoacetanilides appears to be restricted to yellows and oranges. In a previous publication,[3] we reported the correlation between the results of optimised PPP molecular orbital calculations and data obtained from the UV/visible spectra of a range of monoazoacetanilides. We now report an extension of that investigation to a number of disazoacetoacetanilides providing an insight into the relationship between the colour and the molecular structure of these pigments. This study is only a first step in establishing colour and constitution relationships since the colouristic properties of the pigments in application will also show a pronounced dependence on aspects of their solid-state structure such as particle size and shape distribution and the nature of the intermolecular association in the crystal lattice.

2 RESULTS AND DISCUSSION

2.1 Synthesis and structure of the disazoacetoacetanilides

Five disazoacetoacetanilides were prepared by established azo coupling procedures. The series consists of four products of some industrial importance, C.I. Pigment Yellow 12 (**1a**), C.I. Pigment Yellow 83 (**1b**) and C.I. Pigment Orange 16 (**1c**), each of which is prepared from a tetrazotised

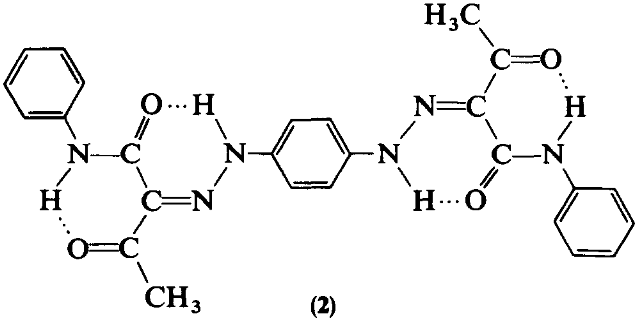


(1)

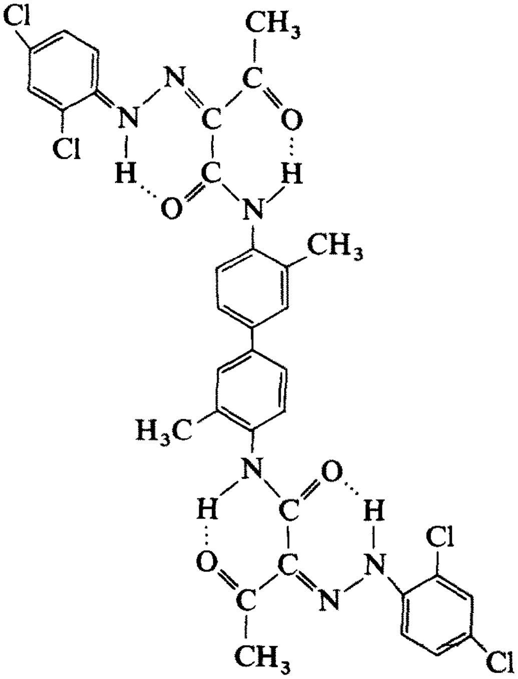
	R^1	R^2	R^3	R^4
1a:	Cl	H	H	H
1b:	Cl	OCH_3	Cl	OCH_3
1c:	OCH_3	H	H	H

benzidine derivative, and C.I. Pigment Yellow 16 (**3**) derived from a bisacetoacetanilide coupling component, together with the previously unreported compound **2** obtained from tetrazotised 1,4-phenylenediamine.

It has been demonstrated conclusively from a series of investigations using a variety of techniques that monoazoacetoacetanilides exist exclusively in the ketohydrazone tautomeric form (**4**) both in solution and in the solid state.[3–13] In spite of their greater commercial significance, the disazoacetoacetanilides have been much less extensively studied probably due to difficulties in applying solution spectroscopic techniques and in growing single crystals suitable for X-ray crystal structure determinations as a result of their extremely low solubilities in most solvents. The solid-state IR spectra of monoazoacetoacetanilides show in each case a single carbonyl absorption in the range 1658–1690 cm^{-1} consistent with the ketohydrazone form (**4**) with extensive intramolecular hydrogen bonding,[3–5] and this has been confirmed in a number of cases by X-ray crystallography.[6–12] The



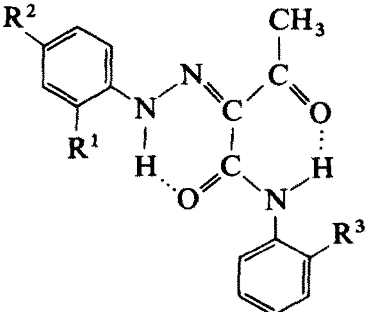
(2)



(3)

disazo pigments **1a–1c**, **2** and **3** gave similar IR spectra to those of the monoazo pigments, showing in each case a single carbonyl absorption in the range 1659–1670 cm^{-1} (Table 1) consistent with their representation as bisketohydrazones analogous to the structures of the monoazo compounds.

Recently, ^{13}C- and ^{15}N-NMR spectroscopy have been used to



(4)

	R^1	R^2	R^3
4a	H	H	H
4b	NO_2	CH_3	H
4c	OCH_3	NO_2	OCH_3

TABLE 1
Infrared Spectral Data and Melting Points

Compound	*C=O stretching frequency (cm^{-1})*	*M.pt (°C) [recrystallising solvent]*
1a	1 667	317 (lit.[15] 317) [DMF]
1b	1 659	369 [1,2,4-Trichlorobenzene]
1c	1 659	345 [1,2,4-Trichlorobenzene]
2	1 661	285 [2-Methoxyethanol]
3	1 670	344 (lit.[15] 325) [DMF]

demonstrate conclusively that a range of monoazoacetoacetanilides, including the parent compound **4a**, exist in solution exclusively in the ketohydrazone form, and definitive assignments of all the signals in the spectra were made.[13] Of the five disazoacetoacetanilides in the present study, only compound **2** had adequate solubility in the usual solvents to allow investigation by NMR spectroscopy. In the ^{13}C spectrum of compound **4a**, the ketone and amide carbonyl signals appear at lowest field (δ 198·9 and 166·6 respectively), the methyl carbon at highest field (δ 25·9) while the $\underline{C}$=N signal appears in the aromatic region of the spectrum.[13] The ^{13}C-NMR spectrum of the disazo pigment **2** is very similar to that of the monoazo derivative **4a**. The presence of ten non-equivalent carbons is indicated, as expected from the symmetry of the molecule, with signals at δ 199·2, 166·3 and 26·0 and the remaining absorptions in the aromatic region. In the ^{1}H-NMR spectrum of compound **4a**, the hydrazone and amide NH protons appear as broad singlets at δ 14·7 and 11·5 ppm respectively. The ^{1}H-NMR spectrum of compound **2** shows similar signals at δ 14·9 and 11·5. These NMR data confirm that compound **2** exists in solution as a symmetrical bisketohydrazone.

2.2 UV/visible spectra

The pronounced differences in the UV/visible spectra of a number of azo dyes, for example 1-phenylazo-2-naphthol,[14] are due to the sensitivity of the position of the enolazo–ketohydrazone equilibrium to changes in solvent. In contrast, the spectra of monoazoacetoacetanilides are relatively insensitive

TABLE 2
Comparison between Experimental and Calculated Values for the Main Absorption Band in the UV/visible Spectra of some Disazoacetoacetanilides

Compound	*Experimental values*						*Calculated valves (PPP–MO method)*	
	Cyclohexane	*DMF*			*1,2,4-Trichlorobenzene*		λ_{max} *(nm)*	f_{osc}
	λ_{max} *(nm)*	λ_{max} *(nm)*	$\varepsilon \times 10^{-4}$ *(litre mol^{-1} cm^{-1})*	$\varepsilon \times 10^{-6}$ *(litre g^{-1} cm^{-1})*	λ_{max} *(nm)*	$\varepsilon \times 10^{-4}$ *(litre mol^{-1} cm^{-1})*		
1a	—[a]	422	6·57	1·04	431	6·87	415	2·47
1b	—[a]	428	—[a]	—[a]	437	—[a]	405	1·87
1c	—[a]	445	5·18	0·84	451	4·99	441	2·52
2	440	442	5·89	1·22	450	5·92	432	1·98
3	—[a]	388	5·33	0·73	399	5·30	382	2·42
4a	374	374	2·75	0·98	381	2·70	376	1·24
4b	403	413	1·86	0·55	417	1·96	442	0·61
4c	410	419	3·77	0·98	423	3·71	420	1·34

[a] Not determined because of insolubility.

to changes in solvent since they exist exclusively in the ketohydrazone form.[3,4] In our previous investigation[3] in which the UV/visible spectral data for some monoazoacetoacetanilides were compared with the results of PPP molecular orbital calculations, DMF was selected as the common solvent because of its ability to dissolve the pigments and because of the relatively small bathochromic shift of the principal absorption band relative to cyclohexane, the solvent on which the generalised set of PPP parameters used was based.

The UV/visible spectral data obtained for the disazo pigments together with the corresponding data for three representative monoazo pigments, the parent compound **4a**, C.I. Pigment Yellow 1 (**4b**) and Pigment Yellow 74 (**4c**), for comparison purposes, are given in Table 2. The principal absorption band in the spectrum of compound **2** obtained from a weak saturated solution in cyclohexane experienced a very small (2 nm) bathochromic shift when the spectrum was recorded in DMF, similar to previous observations with the monoazoacetoacetanilides.[3] A similar comparison with the other disazo pigments **1a**–**1c** and **3**, however, was not possible because of their complete insolubility in cyclohexane. Attempts to obtain a fuller understanding of the influence of the nature of the solvent on the spectra of the series of disazo pigments were limited by the extreme insolubility of the materials in a wide range of solvents investigated. However, the compounds showed reasonable solubility in 1,2,4-trichlorobenzene and the spectral data in this solvent are also given in Table 2. The single visible absorption band in the spectra of the five disazo pigments and of the three monoazo pigments in the aromatic solvent experienced in each case a small bathochromic shift (4–11 nm) relative to DMF. These results are consistent with the existence of the disazo compounds, like the monoazo compounds, exclusively in the ketohydrazone form.

In the monoazoacetoacetanilide series, the position of the absorption band was observed to be influenced considerably more by substituents in the diazo component ring than in the coupling component ring. The disazo pigments **1a**–**1c** show a similar trend in that compound **1b** with two methoxy and one chloro substituents in each coupling component ring gives a λ_{max} only 6 nm higher than that of the correspondingly unsubstituted derivative **1a**, whereas replacement of the two benzidine ring chloro substituents of **1a** with methoxy groups in **1c** results in a bathochromic shift of 23 nm.

The disazo pigments exhibit much larger molar extinction coefficients than the corresponding monoazo derivatives. A comparison of the extinction coefficients, expressed on an equal weight basis (Table 2), arguably a more meaningful practical indication of colour value, reveals that, for example, the disazo Benzidine Yellow C.I. Pigment Yellow 12 (**1a**) offers a considerable colour strength advantage over the classical Hansa

Yellow C.I. Pigment Yellow 1 (**4b**), but shows little advantage in comparison with C.I. Pigment Yellow 74 (**4c**), which is marketed as a superior colour strength monoazo pigment. It is notable that, in the series of pigments investigated, the previously unreported disazo pigment **2** offers the highest colour strength per unit weight.

2.3 PPP molecular orbital calculations

The λ_{max} values calculated using the PPP molecular orbital approach for a range of substituted monoazoacetoacetanilides, after parameter optimisation particularly with respect to the hydrazone grouping, were in good agreement with those obtained experimentally for solutions in DMF.[3] The results of similar calculations using these optimised parameters for the disazoacetoacetanilides together with the results for the three representative monoazo compounds **4a**–**4c** are given in Table 2. For the purposes of these calculations, the molecules were assumed to adopt where appropriate the planar configurations **1**, **2** or **3** with extensive intramolecular hydrogen bonding, analogous to the preferred configuration for the monoazo compounds **4**. The results indicate that even though there are pronounced structural differences in the range of compounds investigated, there is on the whole good agreement between the calculated λ_{max} values and the experimental values for solutions in DMF. In the case of compound **4b**, the somewhat poorer prediction of the λ_{max} value has been attributed previously[3] to the effect of intramolecular hydrogen bonding involving the *o*-nitro group for which no allowance was made in the calculation.

It may be argued convincingly that the prediction of the intensity of the colour of pigments is of even greater practical value than the prediction of λ_{max} values, and this is especially important with these disazo pigments whose main virtue for printing ink applications is their high colour strength. It is of considerable interest therefore that the oscillator strengths calculated by the PPP molecular orbital method for the azoacetoacetanilides show a reasonable qualitative correlation with the experimental molar extinction coefficients obtained for solutions in DMF (Table 2). For example, the higher molar extinction coefficient of C.I. Pigment Yellow 74 (**4c**) ($3{\cdot}71 \times 10^4$ litre mol cm^{-1}), compared with that of the C.I. Pigment Yellow 1 (**4b**) ($1{\cdot}86 \times 10^4$ litre mol cm^{-1}) is reflected in a higher calculated oscillator strength (1·34 for **4c** compared with 0·61 for **4b**). In addition, significantly higher oscillator strengths (1·87–2·52) are calculated for the disazo pigments **1a**, **1c**, **2** and **3**, each of which has a considerably higher molar extinction coefficient [$(5{\cdot}1\text{–}6{\cdot}6) \times 10^4$ litre mol cm^{-1}] than the monoazo derivatives. Compound **1b** had insufficient solubility to allow its molar extinction coefficient to be determined.

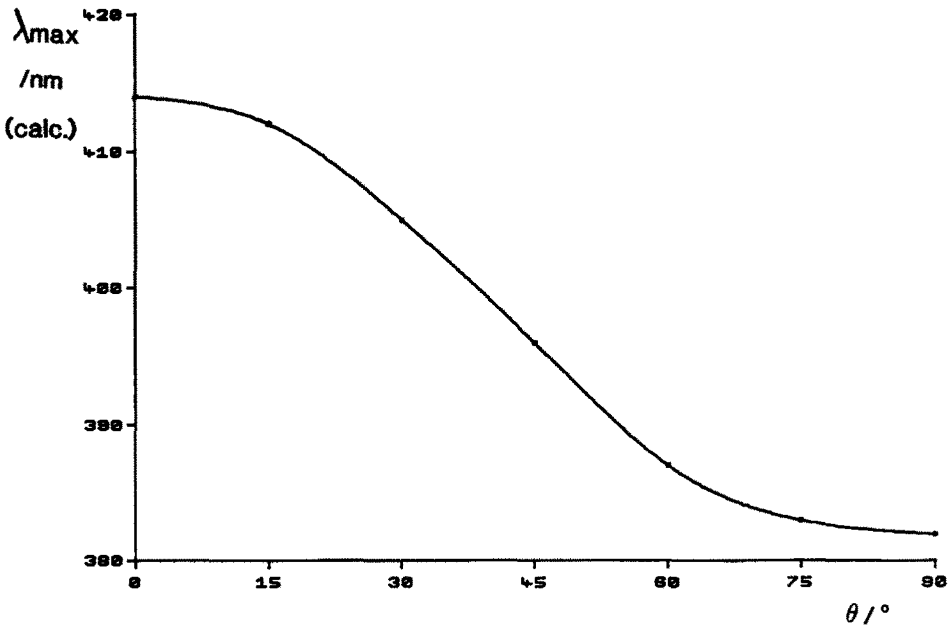


Fig. 1. Variation in the predicted λ_{max} value (PPP–MO method) with angle of twist (θ) of the biphenyl ring system in C.I. Pigment Yellow 12.

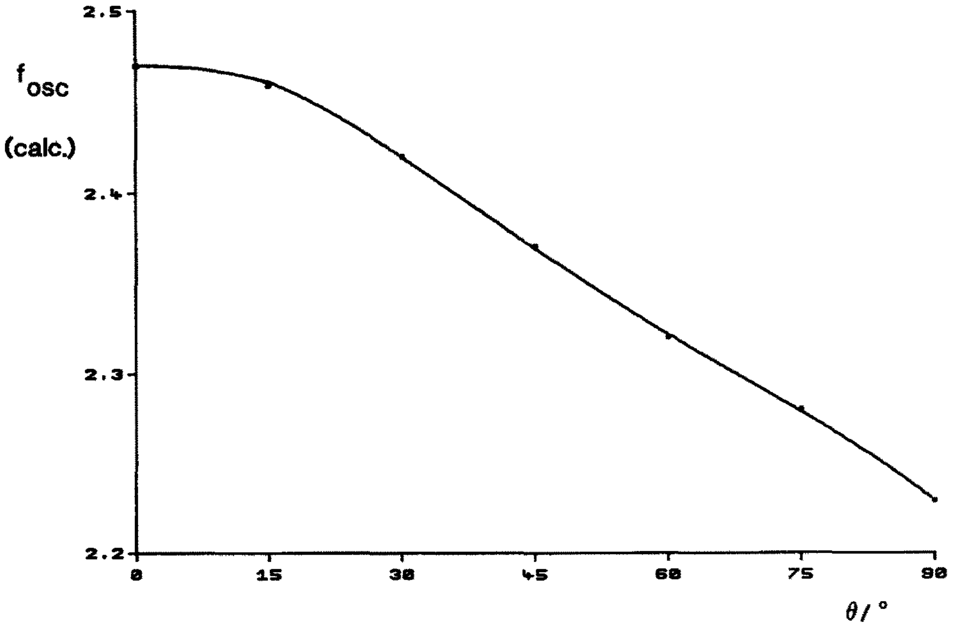
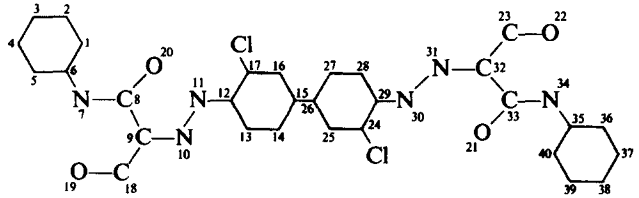


Fig. 2. Variation in the calculated oscillator strength value (PPP–MO method) with angle of twist (θ) of the biphenyl ring system in C.I. Pigment Yellow 12.

The assumption of planar molecular geometry for the PPP molecular orbital calculations carried out on the disazo pigments may well be correct for compound **2**, but it is rather less certain for compounds **1a–1c** and **3**, each of which is a derivative of biphenyl. Biphenyl itself is planar in the crystalline solid state,[16] but the rings are inclined at an angle of 42° in the gas phase[17] and at a somewhat smaller angle in solution.[18] Calculations have in fact shown that the energy of the molecule is relatively insensitive to rotation about the formal single bond between the rings through a wide range of torsion angle[19] and it might be expected that a similar situation would exist with substituted biphenyls such as the aforementioned disazo pigments. An empirical correction for non-planarity which has been used in PPP molecular orbital calculations involves the replacement of the bond

TABLE 3

Calculated π-Electron Densities for C.I. Pigment Yellow 12 (**1a**)



Atom	π-Electron density	
	Ground state	First excited state
1, 40	1·02	1·01
2, 39	1·00	1·00
3, 38	1·03	1·02
4, 37	1·00	1·00
5, 36	1·05	1·05
6, 35	1·00	1·00
7, 34	1·65	1·64
8, 33	0·77	0·78
9, 32	1·08	1·04
10, 31	1·08	1·21
11, 30	1·51	1·42
12, 29	0·99	0·99
13, 28	1·05	1·02
14, 27	0·98	0·98
15, 26	1·02	0·99
16, 25	0·96	0·94
17, 24	1·11	1·10
18, 23	0·70	0·75
19, 22	1·45	1·47
20, 21	1·58	1·58

resonance integral β with $\beta \cos \theta$ where θ is the angle of twist about that particular bond.[20] The variation in the λ_{max} and oscillator strength values with the biphenyl torsion angle calculated for C.I. Pigment Yellow 12 (**1a**) using this correction are illustrated in Figs 1 and 2 respectively. As the bond is rotated from 0 to 90°, a progressive hypsochromic shift and reduction in oscillator strength are predicted, presumably as a result of the disruption in the conjugation which occurs. The best correlation with the experimental λ_{max} for this compound (422 nm) is given assuming planar geometry for the molecule.

The π-electron charge densities calculated for the ground and first excited states of compound **1a** are given in Table 3. The results indicate that the symmetry of the molecule about the biphenyl link (C-20/C-21) is retained in the excitation process which involves principally an increase in the charge densities on N-10 and N-31 and a decrease in the charge densities on N-11 and N-30, a mechanism analogous to that calculated previously for the parent monoazoacetoacetanilide (**4a**).[3]

3 CONCLUSION

The λ_{max} values for a series of symmetrical disazoacetoacetanilide pigments calculated by the PPP molecular orbital method using a generalised set of parameters optimised previously for a series of monoazoacetoacetanilides give a good correlation with λ_{max} values obtained experimentally for the principal absorption band in the UV/visible spectra of the compounds in DMF solutions, assuming that the compounds exist as bisketohydrazones with planar molecular geometry. On the basis of calculated oscillator strengths, the PPP molecular orbital method also successfully predicts the increased molar extinction coefficients of the disazo pigments compared with the corresponding monoazo derivatives. The method offers considerable potential for the prediction of the colouristic properties of new synthetic target molecules of potential interest as pigments, such as unsymmetrical disazo pigments, few of which have been previously reported, and pigments derived from novel carbocyclic or heterocyclic diamines.

4 EXPERIMENTAL

4.1 Instrumental methods

Infrared spectra were recorded as KBr discs with a Perkin–Elmer 599B spectrophotometer. Melting points are extrapolated onset temperatures obtained using a Mettler DSC30 differential scanning calorimeter with a heating rate of $5\,\mathrm{K\,min^{-1}}$ and a flowing nitrogen atmosphere. UV/visible spectra were recorded on a Pye–Unicam SP8-200 spectrophotometer interfaced with an Apple microcomputer. ^{1}H-NMR spectra were recorded on a Perkin–Elmer spectrophotometer for solutions in $CDCl_3$ using tetramethylsilane as internal reference. ^{13}C-NMR spectra were recorded on a Brooker WP200 instrument for solutions in $CDCl_3$.

4.2 PPP molecular orbital calculations

A standard PPP–MO procedure was used within the fixed β approximation.[20] Two-centre repulsion integrals were determined by the Nishimoto–Matago relationship[21] 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 Synthesis of the disazoacetoacetanilides

Compounds **1a**–**1c** and **3** were prepared by well-established procedures.[3] Samples of the pigments were purified by recrystallisation and their purity established by thin-layer chromatography.

Compound **2** was synthesised by tetrazotisation of *p*-phenylenediamine (2·16 g, 0·02 mol) in orthophosphoric acid with nitrosylsulphuric acid using an established procedure,[22] and subsequent coupling of the resulting tetrazonium salt with acetoacetanilide (0·046 mol) using the standard procedure previously described.[3] Compound **2** (8·36 g, 43%) was obtained as a reddish-yellow powder. (Found: C, 64·6; H, 4·8; N, 17·2. $C_{26}H_{24}N_6O_4$ requires: C, 64·4; H, 5·0; N, 17·4%). δ_H 2·62 (6H, s, CH_3), 7·10–7·90 (14H, m, ArH), 11·48 (2H, br s, amide NH), 14·90 (2H, br s, hydrazone NH). δ_C 26·0 (CH_3), 117·0, 121·0, 124·8, 126·2, 129·0, 137·0, 139·0 (aromatic carbons and C=N), 163·0 (CONH), 199·2 ($\underline{C}OCH_3$).

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