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Colour and Constitution Relationships in Organic Pigments. Part 1—Monoazoacetoacetanilides

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SUMMARY

Monoazoacetoacetanilides provide some of the most important classical organic pigments in the yellow to orange shade area for a range of applications. As a first step in attempting to establish the colour and constitution relationships in this series of products, a range of monoazoacetoacetanilides was synthesised and their UV/visible spectral behaviour in solution investigated. PPP molecular orbital calculations, using the generalised set of parameters approach, were refined by parameter optimisation to provide an excellent correlation between calculated and experimental λ_{max} values for the principal absorption band, and in addition there was generally good qualitative agreement between molar extinction coefficients and the calculated oscillator strengths. The nature of the electronic excitation process is discussed in terms of the calculated changes in π-electron charge densities.

1 INTRODUCTION

In the range of classical organic pigments, by far the most important yellow products are azo pigments derived from acetoacetanilide coupling

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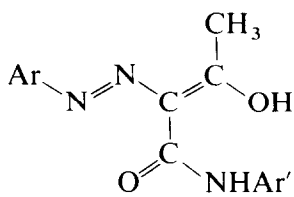
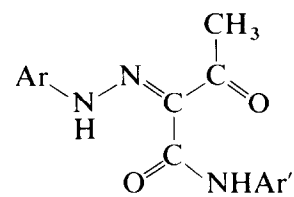
components. The monoazoacetoacetanilides are traditionally known as Hansa Yellows and constitute one of the longest-established ranges of organic pigments, a number of derivatives having achieved some commercial significance over the years.[1] Currently amongst the most important commercially are C.I. Pigment Yellow 1 (Hansa Yellow G) and C.I. Pigment Yellow 3 (Hansa Yellow 10G), two of the earliest products, together with the somewhat more recently introduced product C.I. Pigment Yellow 74. These classical Hansa Yellows are characterised by their good lightfastness but relatively poor solvent resistance and they find their principal use today in decorative paint applications. For other applications, and especially printing inks, the structurally-related disazoacetoacetanilides (Benzidine Yellows) are preferred because of their higher colour strength and enhanced solvent-fastness properties. Two benzimidazolone monoazoacetoacetanilides, C.I. Pigment Yellow 120 and C.I. Pigment Orange 36, exhibit a range of excellent fastness properties, attributed principally to the enhanced stability which results from extensive intermolecular hydrogen bonding involving the benzimidazolone ring system, and these products are suitable for use in more demanding paint and plastics applications.

Whilst most texts illustrate the structures of the monoazoacetoacetanilides by convention in an enolazo form such as (**1a**), there is considerable evidence from UV/visible and infrared spectral data that the compounds exist exclusively in the ketohydrazone form (**1b**) both in the solution and in



(1a)



(1b)

the solid state phases.[2,3] A number of single-crystal X-ray diffraction studies have confirmed this observation for the solid state[4-11] whilst a recent investigation involving ^{13}C- and ^{15}N-NMR spectroscopy has provided similar confirmation for the solution phase.[12]

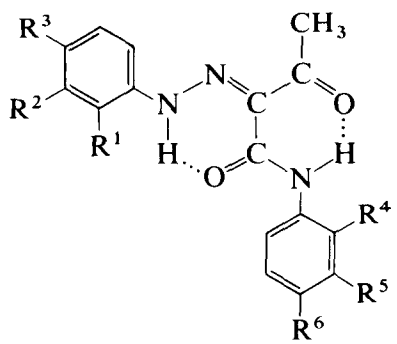
In common with other hydrazone colourants, the colours of the monoazoacetoacetanilides appear to be restricted to yellows and oranges. In this paper we report an investigation into the relationship between the colour and the molecular structure of a range of monoazoacetoacetanilide pigments, in which the results of PPP molecular orbital calculations are correlated with the data obtained from UV/visible spectra of the materials in solution. It is recognised, of course, that since pigments are applied in a solid-

state particulate form, the colour observed in application will be dependent not only on the molecular structure but also on the nature of the intermolecular association in the crystal lattice and on aspects of the physical form of the pigment such as particle size and shape distribution and the degree of aggregation. The present study therefore must be considered as only the first step in establishing fully the colour and constitution relationships in this series of pigments.

2 RESULTS AND DISCUSSION

2.1 Synthesis and structure of the monoazoacetoacetanilides

A range of monoazoacetoacetanilides, **2a–2l**, was prepared using well-established azo coupling procedures. This series includes the parent compound (**2a**) together with a number of derivatives, **2b–2i**, selected to allow investigation of the influence of methoxy and nitro substituents, as



(2)

Compound	R^1	R^2	R^3	R^4	R^5	R^6
2a	H	H	H	H	H	H
2b	CH_3O	H	H	H	H	H
2c	H	CH_3O	H	H	H	H
2d	H	H	CH_3O	H	H	H
2e	H	H	H	CH_3O	H	H
2f	NO_2	H	H	H	H	H
2g	H	NO_2	H	H	H	H
2h	H	H	NO_2	H	H	H
2i	H	H	H	H	H	NO_2
2j	NO_2	H	CH_3	H	H	H
2k	CH_3O	H	NO_2	CH_3O	H	H
2l	NO_2	H	Cl	H	—NHCONH—	

representative examples of electron-releasing and electron-withdrawing groups respectively, in a range of positions both in the diazo and coupling component rings on the UV/visible spectral properties of the pigments. The set is completed with the inclusion of three products of current commercial importance, C.I. Pigment Yellow 1 (**2j**), C.I. Pigment Yellow 74 (**2k**) and the benzimidazolone derivative C.I. Pigment Orange 36 (**2l**).

The infrared spectra of azoacetoacetanilides, and in particular the position of the carbonyl stretching frequencies, have been of considerable importance in establishing that the compounds exist exclusively in the ketohydrazone form. In a previous publication, the spectrum of the parent compound (**2a**) in the solid state was reported to show two carbonyl absorptions at 1667 and 1623 cm^{-1} attributed to the amide and ketone groups respectively.[2] A similar spectrum was reported for solutions of the compound. However, in a recent more definitive study[3] involving a comparison of the IR spectrum of compound **2a** with the spectra of a number of *N*-methyl analogues, the compound was reported to show a single carbonyl absorption band at 1669 cm^{-1} attributed by the authors to overlap of the bands due to the amide and ketone functionalities. This is consistent with published data for these groups when involved in strong intramolecular hydrogen bonding as is suggested in this case.[13] The carbonyl stretching frequencies obtained from the IR spectra of compounds **2a**–**2l** are given in Table 1 together with the observed melting point data. Compounds **2a**–**2k** each showed a single carbonyl absorption in the range 1658–1671 cm^{-1}, consistent in each case with the ketohydrazone tautomeric

TABLE 1
IR Spectral Data and Melting Points

Compound	*C=O stretching frequency* (cm^{-1})	*Recrystallising solvent*	*M.p.* (°C)
2a	1 663	Ethanol	107·5 (lit.[14] 107–108)
2b	1 658	Ethanol	140·0 (lit.[14] 139–140)
2c	1 663	Ethanol	96·0
2d	1 660	Ethanol	128·0 (lit.[14] 126–127)
2e	1 664	Ethanol	144·0
2f	1 671	2-Methoxyethanol	206·0 (lit.[14] 206–207)
2g	1 665	2-Methoxyethanol	196·5 (lit.[14] 196–197)
2h	1 664	2-Methoxyethanol	213·5 (lit.[14] 215–216)
2i	1 658	2-Methoxyethanol	226·0
2j	1 665	DMF	260·5 (lit.[15] 256)
2k	1 671	DMF/acetic acid	294·5 (lit.[15] 293)
2l	1 690 1 745	DMF	367·0 (decomp.)

form with strong intramolecular hydrogen bonding. The benzimidazolone derivative (**2l**) was found to absorb at a somewhat higher frequency ($1690\,cm^{-1}$). This may be due to the participation of the carbonyl groups in intermolecular, in addition to the usual intramolecular, hydrogen bonding in derivatives of this type, as has been demonstrated for one particular compound by X-ray crystallography.[11] A second absorption at $1745\,cm^{-1}$ in the spectrum of compound **2l** is attributed to the benzimidazolone ring carbonyl group.

2.2 UV/visible spectra

It has long been established that the UV/visible spectrum of 1-phenylazo-2-naphthol shows marked differences depending on the solvent used and that this is due to the extreme sensitivity of the position of the equilibrium between enolazo and ketohydrazone forms to changes in solvent.[16] In contrast, the position and intensity of the principal absorption band in the UV/visible spectrum of compound **2a** has been shown to be relatively insensitive to changes in solvent, consistent with the existence of a single tautomeric form.[2] Some UV/visible spectral data for substituted monoazoacetoacetanilides may be found in the earlier literature,[13,17] but it was thought appropriate for the purposes of the present study to investigate the spectra of the complete series of compounds **2a–2l** in a suitable common solvent.

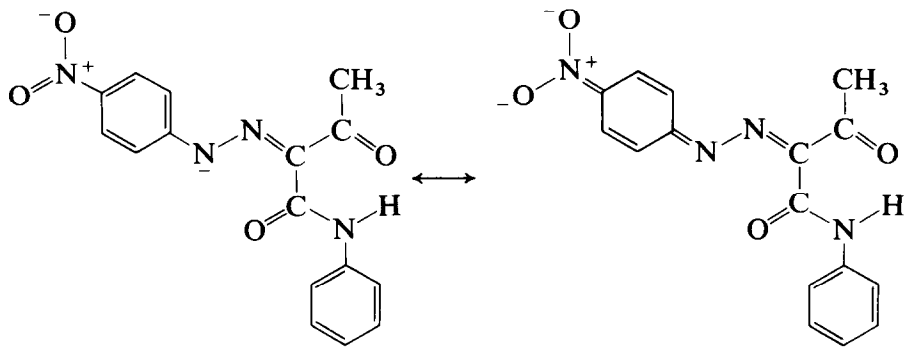
Table 2 shows the λ_{max} values and molar extinction coefficients obtained for solutions of compounds **2a–2i** in cyclohexane, the preferred solvent for an investigation whose aim was to correlate the spectral data with the results of PPP molecular orbital calculations, using a parameter set optimised for spectra in this solvent. Compounds **2j–2l**, however, had inadequate solubility in cyclohexane to allow evaluation of molar extinction coefficients, although λ_{max} values for weak saturated solutions are quoted. Also given in Table 2 are the spectral data obtained for solutions, in the more powerful solvent DMF, in which each of the compounds had adequate solubility. Because of absorption by DMF, bands below 280 nm were not observed. In the case of compounds **2h** and **2k**, each of which contains a *p*-nitro substituent, it was necessary to add to the DMF a small amount (0·5%) of acetic acid to suppress formation of the anion (**3**) whose presence resulted in the appearance of an additional absorption band at higher wavelength. The relative ease of formation of the anion **3** from these compounds may be attributed to the additional resonance stabilisation which results from delocalisation of the negative charge on to the *p*-nitro group. Compounds **2a–2l** in DMF (or DMF–acetic acid) in each case gave a linear Beer's Law correlation. In agreement with previous observations,[2] the position of the

TABLE 2
UV/Visible Spectral Data

Compound	*Cyclohexane solution*		*DMF solution*	
	λ_{max} (*nm*)	$\varepsilon_{max} \times 10^{-4}$ (*litre mol*$^{-1}$ *cm*$^{-1}$)	λ_{max} (*nm*)	$\varepsilon_{max} \times 10^{-4}$ (*litre mol*$^{-1}$ *cm*$^{-1}$)
2a	374	2·88	374	2·75
	262	1·29		
	252	1·64		
	243	1·65		
2b	389	2·71	392	2·78
	255	1·49		
	244	1·51		
	237	1·14		
2c	379	2·81	377	2·66
	264	1·60		
2d	390	2·96	392	2·77
	305	0·58		
	259	1·40		
	238	1·63		
2e	377	2·90	378	2·85
	270	1·24		
	251	1·45		
2f	396	2·47	404	1·99
	337	1·53	338	1·59
	251	1·96		
2g	372	2·78	381[c]	2·35
			331[c]	
2h	388	3·96	393[b]	3·95
	250	1·56		
	245	1·57		
2i	380	3·10	385	3·58
	318	1·46		
	252	1·00		
2j	403[a]		413	1·86
	344		343	1·54
	254			
2k	410[a]		419[b,c]	3·77
	276			
2l	410[a]		416	1·29
	275		348	1·44

[a] Spectrum of saturated solution in cyclohexane; insufficient solubility to allow evaluation of molar extinction coefficients.
[b] Spectrum recorded in DMF/0·5% acetic acid.
[c] First-order spectrum shows a single broad absorption resolved into two bands in the second derivative.

main absorption band in the spectrum of the parent compound (**2a**) was essentially the same in cyclohexane as in the much more polar solvent DMF (Fig. 1), whilst solvent shifts of only 1–2 nm were observed for the methoxy derivatives **2b–2e**. Compounds **2f–2l**, each of which contains a nitro substituent, showed positive solvatochromism but the shifts were sufficiently small (5–10 nm) and consistent to provide justification of the attempt to correlate the data obtained from spectra in DMF with the results of PPP molecular orbital calculations based on parameters optimised for spectra in cyclohexane.



(3)

Incorporation of a methoxy or a nitro substituent into the monoazoacetoacetanilide system gives rise to a bathochromic shift of the principal absorption maximum. In general, however, the shifts are rather small. The largest shift (30 nm) is produced by a nitro substituent in the *ortho*-position of the diazo component ring while *o*-methoxy, *p*-nitro and *p*-methoxy substituents in that ring give rise to shifts of 18–20 nm. Substituents in the coupling-component ring or in the *meta*-position in the diazo-component ring give somewhat smaller shifts. An interesting observation is that the presence of a *p*-nitro group, either in the diazo component or coupling-component ring, gives rise to a pronounced increase in the molar extinction coefficient. In contrast, an *o*-nitro group in the diazo-component ring reduces the extinction coefficient. Methoxy and *m*-nitro substituents appear to have little effect on the absorption intensities.

The spectra of the *o*-nitro derivatives (**2f**) (Fig. 2), **2j** and **2k** in DMF show an additional absorption band in the 330–350 nm region. The spectrum of the *m*-nitro derivative **2g** (Fig. 3) shows a single broad absorption which may be resolved into two separate bands (λ_{max} 331 and 381 nm) corresponding to the two minima in the second derivative of the spectrum (Fig. 4).

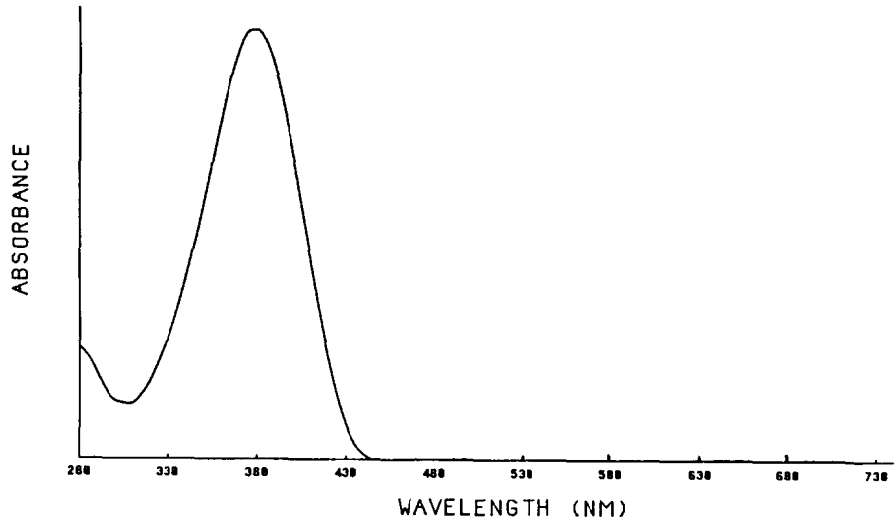


Fig. 1. UV/visible spectrum of **2a** in DMF.

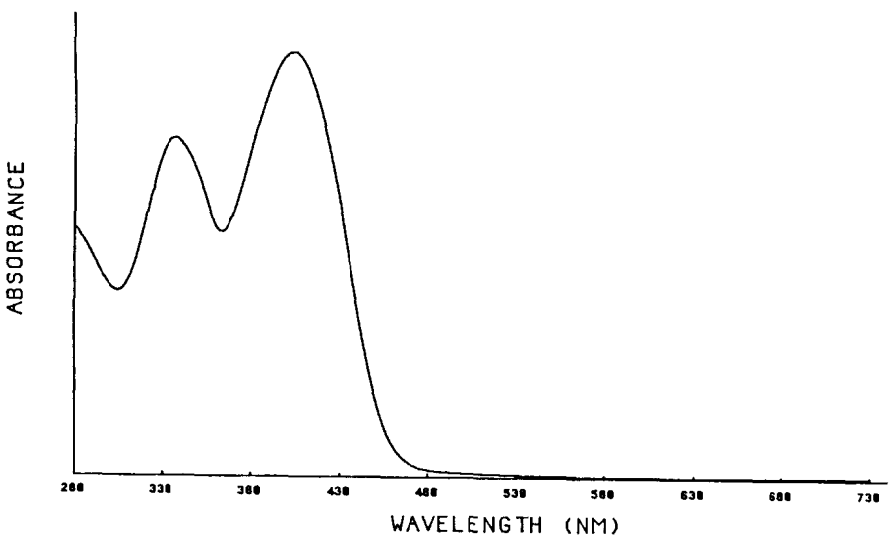


Fig. 2. UV/visible spectrum of **2f** in DMF.

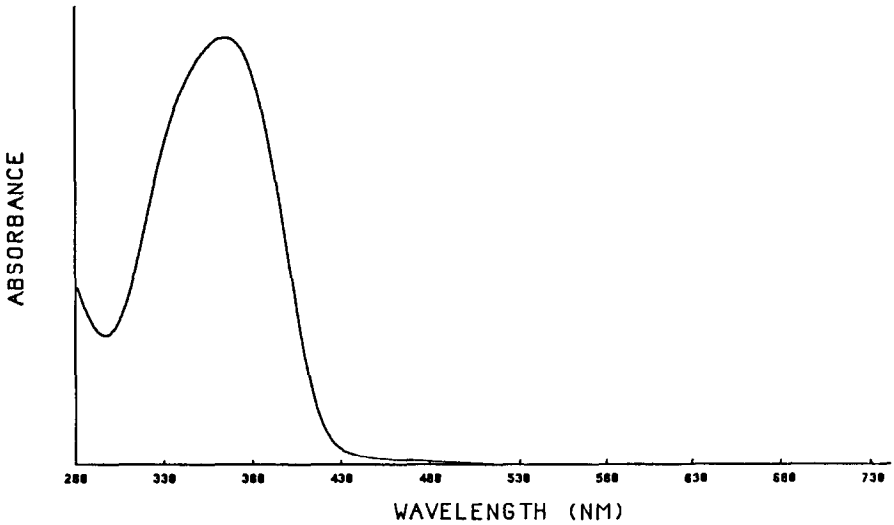


Fig. 3. UV/visible spectrum of **2g** in DMF.

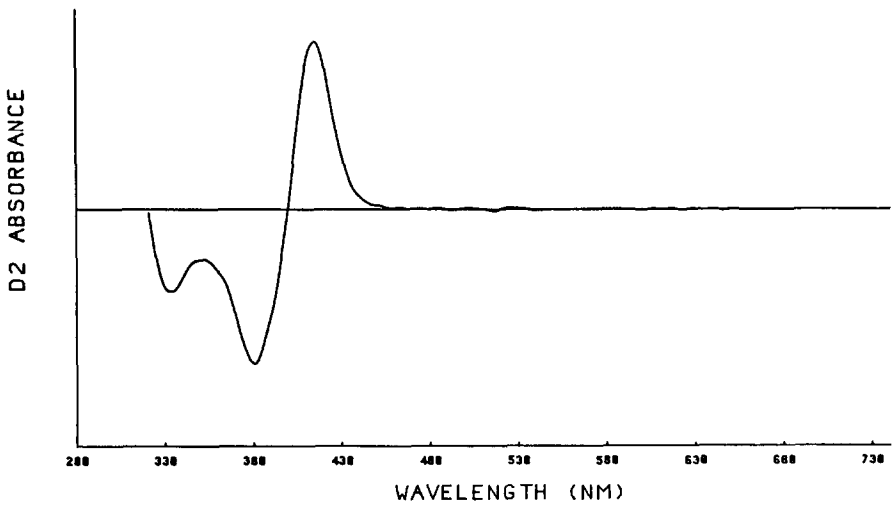


Fig. 4. UV/visible spectrum of **2g** in DMF (second derivative).

2.3 PPP molecular orbital calculations

The use of the Pariser–Pople–Parr (PPP) molecular orbital method to account for the UV/visible spectra of organic colourants is now well-established. In particular, an approach using a generalised set of parameters has proved very successful in predicting the λ_{max} values of a range of chromophoric systems to a reasonable degree of accuracy, while refinement of the calculations by parameter optimisation can provide excellent correlation between experimental and calculated λ_{max} values within a particular class of colourants.[18,19] In addition, the calculated oscillator strength values may be used to predict molar extinction coefficients. The PPP method using the generalised parameter approach has been applied successfully to a few hydrazone dyes,[20,21] whilst the method in Dewar's form has been used to account theoretically for the UV/visible spectral properties of the parent azoacetoacetanilide (**2a**).[22]

We now report the results of an investigation into the application of the PPP MO approach using the generalised set of parameters to a range of substituted monoazoacetoacetanilides. In this study a standard PPP MO procedure was employed within the fixed-β approximation.[19] Two-centre repulsion integrals were determined by the Nishimoto–Mataga relationship[23] 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.

X-ray crystallography has been used to demonstrate that the monoazoacetoacetanilides in the crystalline solid state adopt the essentially planar configuration (**2**) with extensive intramolecular hydrogen-bonding.[4–11] It has been confirmed recently[12] that this is also the preferred configuration in solution on the basis of ^{15}N–^{13}C coupling constants obtained from ^{13}C spectra of some ^{15}N-labelled derivatives. The molecular geometry of this configuration was therefore assumed for the purpose of the calculations. Substituents in the *o*-positions were assumed to be fixed by intramolecular hydrogen bonding in the conformation shown, while for *m*-substituted derivatives calculations were carried out for the two possible positions of the substituent and the results averaged.

The set of generalised PPP parameters used initially are given in Table 3,[18,24,25] and the results of the molecular orbital calculations based on these original parameters are shown in Table 4. The λ_{max} values calculated from these parameters are seen to be some 40–50 nm higher than the experimental values. However, the values showed the expected trends and it appeared likely that the correlation might be improved by optimising the parameters.

In the empirical approach to parameter optimisation adopted, some trial

TABLE 3
Generalised Set of PPP MO Parameters for Calculation of UV/Visible Absorption Spectral Data[18,19,25]

Bond type (*X*—*Y*)	r_{X-Y}[a] (Å)	β_{X-Y}[b] (*eV*)	$VSIP_Y$[c] (*eV*)	A_Y[d] (*eV*)	Z_Y[e] (*eV*)
Aromatic					
C—C	1·40	−2·39	11·16	0·03	1
Cl—C[f]	—	—	12·00	0·61	1
Carbonyl					
C—C=	1·45	−2·30	11·16	0·03	1
C=O (H-bonded)	1·22	−2·46	17·70	2·47	1
Hydrazone					
C=N	1·33	−2·48	15·00	0·97	1
=N—NH (H-bonded)	1·35	−2·42	18·00	8·50	2
NH—C	1·40	−2·75	11·16	0·03	1
Nitro					
N—O	1·21	−2·80	21·00	2·50	1
C—N	1·49	−2·00	24·80	12·50	2
Methoxy					
C—OCH_3	1·36	−2·60	32·90	11·40	2
Amide					
C—NH	1·38	−2·75	21·9	10·15	2
π-excessive heterocyclic N					
C—N	1·35	−2·40	21·00	10·00	2

[a] Bond length.
[b] Bond resonance integral.
[c] Valence state ionisation potential of atom Y.
[d] Electron affinity of atom Y.
[e] Core charge of atom Y.
[f] Modified to simulate the inductive effect of Cl.

calculations were carried out by systematically varying the valence state ionisation potentials, electron affinities and bond β values for each of the heteroatomic centres in the molecules while leaving the bond lengths and angles and the parameters for the carbon atoms unchanged. In general it was found that the calculations were more sensitive to changes in the parameters involving the hydrazone nitrogen atoms than those involving the amide and carbonyl functions. In particular, it was found that the desired hypsochromic shift of the calculated λ_{max} values could be achieved by modifying the parameters for the hydrazone group to those shown in Table 5. In addition, it was found advantageous to adjust the nitro N—O bond β value from −2·80 to −3·05 eV, a value which had been suggested previously.[18] The λ_{max} values calculated using these modified parameters (Table 4) are now mostly in excellent agreement with the experimental data. With the exception of compounds **2f** and **2l** the calculated values are within 5 nm of those

TABLE 4
Comparison Between Experimental and Calculated Values for the Main Absorption Band in the UV/Visible Spectra of some Monoazoacetoacetanilides

Compound	*Experimental values (DMF)*		*Calculated values*			
	λ_{max} (*nm*)	$\varepsilon \times 10^{-4}$ (*litre mol*$^{-1}$ *cm*$^{-1}$)	*Original parameters*		*Modified parameters*	
			λ_{max} (*nm*)	f_{osc}	λ_{max} (*nm*)	f_{osc}
2a	374	2·75	418	1·27	376	1·24
2b	392	2·78	432	1·28	393	1·22
2c	377	2·66	420	1·30	378	1·27
2d	392	2·77	427	1·33	387	1·27
2e	378	2·85	420	1·30	380	1·19
2f	404	1·99	490	0·71	442	0·61
2g	381	2·35	414	1·20	378	0·73
2h	393	3·95	449	1·50	396	1·45
2i	385	3·56	427	1·26	383	1·25
2k	419	3·77	462	1·43	420	1·34
2l	416	1·29	482	0·75	433	0·63

measured experimentally. These exceptions may well be due to the effect of intramolecular hydrogen bonding involving the *o*-nitro group for which no allowance was made in the calculation.

The prediction of intensity of colour is arguably of even more value with pigments than the prediction of λ_{max} values. It is of considerable interest therefore that the oscillator strengths calculated using the modified PPP parameters (Table 4) show a reasonable qualitative correlation with the experimental molar extinction coefficients. For example, similar oscillator strengths (1·19–1·27) are calculated for the parent compound **2a** and the methoxy derivatives **2b–2e**, all of which show similar molar extinction coefficients [(2·66–2·85) $\times 10^4$ litre mol^{-1} cm^{-1}]. The higher molar extinction coefficients (3·95 $\times 10^4$ and 3·77 $\times 10^4$ litre mol^{-1} cm^{-1}) shown

TABLE 5
Optimised PPP MO Parameters for the Azoacetoacetanilides Hydrazone Group

Bond type (*X—Y*)	r_{X-Y} (*Å*)	β_{X-Y} (*eV*)	$VSIP_Y$ (*eV*)	A_Y (*eV*)	Z_Y (*eV*)
C=N	1·33	−2·70	13·69	0·97	1
=N—NH (H-bonded)	1·35	−2·63	19·58	9·25	2
NH—C	1·40	−2·75	11·16	0·03	1

by the *p*-nitro derivatives **2h** and **2k** are reflected in the calculated oscillator strengths (1·45 and 1·38 respectively). This observation is of some industrial consequence in that a particular feature of C.I. Pigment Yellow 74 (**2k**) in application is its high colour strength, which these results indicate is probably due in the main to the presence of a nitro group in the *p*-position of the diazo-component ring. The calculations also successfully predict the somewhat lower molar extinction coefficients of the *o*-nitro derivatives **2f** and **2l**, although the method fails to account for the higher extinction coefficient obtained for compound **2i**, which contains a *p*-nitro group in the coupling-component ring.

The results contained in Table 6 show that the PPP MO calculations predict to a reasonable degree of accuracy the lower-wavelength absorptions observed in the UV/visible spectrum of compound **2a** in cyclohexane and in the spectra of the nitro-substituted derivatives **2f**, **2g** and **2l** in DMF.

The calculated π-electron charge densities for both the ground state and first excited state of the parent compound **2a** are shown in Table 7. The ground-state charge densities are in accord with the valence-bond description of the bonding in compound **2a** given in Fig. 5. For example, there is a decrease in charge density on the two π-excessive N-atoms, more pronounced on the hydrazone nitrogen (N-5) than on the amide nitrogen (N-9), while an increase in charge density is observed on the O-atoms, more pronounced on the amide oxygen (O-14) than on the ketone

TABLE 6

Comparison Between Experimental and Calculated Data for Additional Absorption Bands in the UV/Visible Spectra of some Monoazoacetoacetanilides

Compound	*Experimental values*		*Calculated values (using modified PPP parameters)*	
	λ_{max} (*nm*)	$\varepsilon_{max} \times 10^{-4}$ (*litre mol*$^{-1}$ *cm*$^{-1}$)	λ_{max} (*nm*)	f_{osc}
2a[a]	262	1·29	265	0·36
	252	1·64	250	0·20
	243	1·65	236	0·16
2f[b]	338	1·59	344	0·69
2g[b]	331[c]	—[c]	367	0·70
2l[b]	348	1·44	340	0·65

[a] For cyclohexane solutions.

[b] For DMF solutions.

[c] Obtained from the second derivative, so that molar extinction coefficient could not be calculated.

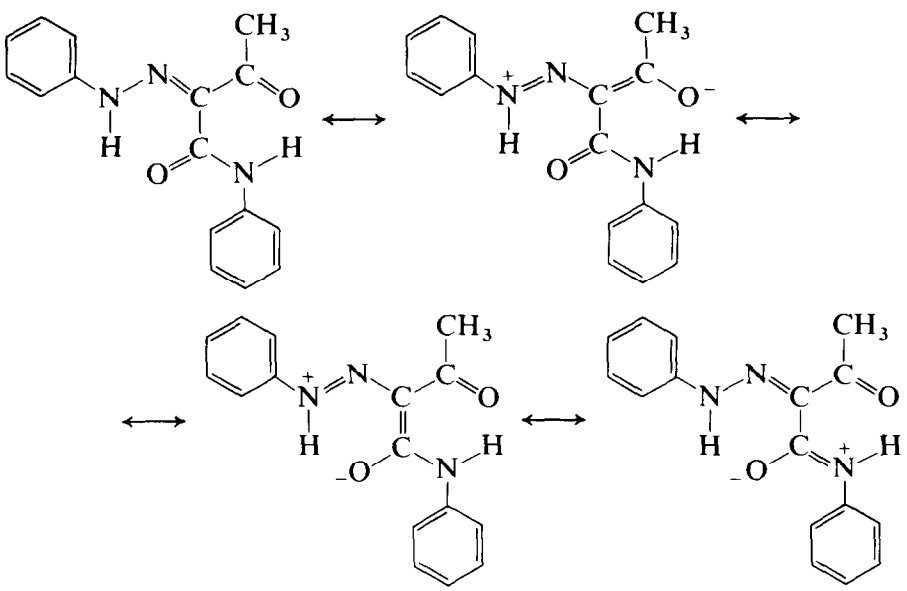


Fig. 5. Canonical forms of compound **2a**.

oxygen (O-16). Electronic excitation produces increased polarisation resulting in a further decrease in charge densities on N-5 and N-9 and further gains in charge density by the O-atoms. However, the most notable feature of the excited state which cannot be easily explained by traditional valence-bond representations is the pronounced increase in charge density on N-6. An examination of the calculated π-electron charge densities for the ground and excited states of the substituted derivatives **2b–2l** indicates that in each case the highest-wavelength absorption band in the spectrum is due to an electronic excitation similar to that observed in the case of the parent compound (**2a**). For compound **2g** the charge density on the *m*-nitro group remains virtually unaffected by the excitation. The second absorption band in the spectrum of **2g** appears to be due to an electronic transition which involves principally a decrease in charge on the π-excessive nitrogens (N-5 and N-9) and an increase in charge on the atoms of the nitro group.

The first electronic transition in the case of compounds **2f** and **2h**, each of which contains a nitro group conjugated with the chromophoric system, is characterised by a similar charge transfer pattern to that given by **2a**, although somewhat smaller in magnitude, but in addition there is an increase in charge density on the atoms of the nitro group. The electronic transition giving rise to the second absorption band in the spectrum of the *o*-nitro derivative (**2f**) is suggested to be due to the formation of a second excited state which differs from the first principally in showing a more pronounced increase in charge on N-6.

TABLE 7
Calculated π-Electron Densities for Parent Compound **(2a)**

Atom	*π-electron density*	
	Ground state	*1st excited state*
1	1·01	0·98
2	0·99	0·99
3	1·04	1·01
4	1·01	1·01
5	1·51	1·36
6	1·08	1·38
7	1·08	0·98
8	0·77	0·80
9	1·65	1·59
10	1·00	0·97
11	1·05	1·03
12	1·00	1·00
13	1·02	0·99
14	1·58	1·61
15	0·69	0·84
16	1·45	1·49

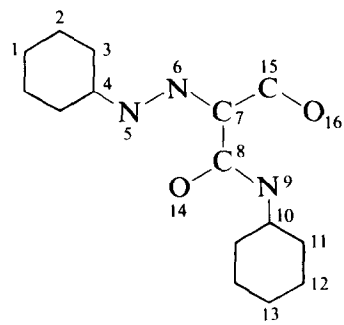
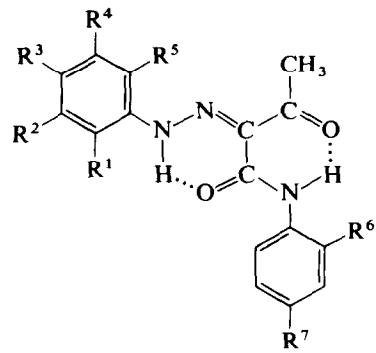


Fig. 6. Numbering of atoms listed in Table 7 for compound **2a**.

The nitro derivatives **2f** and **2h–2l** show more pronounced positive solvatochromism than compounds **2a–2e** (Table 2). This is consistent with the larger difference between the dipole moment of the first excited state and that of ground state calculated by the PPP molecular orbital method for those nitro compounds. For example, a ground-state dipole moment of 3·50D and a first-excited-state dipole moment of 5·08D are calculated for the parent compound **2a**, while for the *p*-nitro derivative **2h** ground-state and excited-state dipole moments of 2·40D and 23·43D respectively are calculated.

TABLE 8
PPP MO Predictions for some Monoazoacetoacetanilides



(4)

Compound	R^1	R^2	R^3	R^4	R^5	R^6	R^7	λ_{max}(*calc.*) (*nm*)	f_{osc}
4a	CH_3O	CH_3O	H	H	H	H	H	391	1·16
4b	CH_3O	H	CH_3O	H	H	H	H	402	1·24
4c	CH_3O	H	H	CH_3O	H	H	H	402	1·21
4d	CH_3O	H	H	H	CH_3O	H	H	406	1·15
4e	H	CH_3O	CH_3O	H	H	H	H	391	1·27
4f	H	CH_3O	H	CH_3O	H	H	H	377	1·18
4g	CH_3O	H	CH_3O	H	CH_3O	H	H	414	1·19
4h	NO_2	NO_2	H	H	H	H	H	435	0·56
4i	NO_2	H	NO_2	H	H	H	H	431	0·84
4j	NO_2	H	H	NO_2	H	H	H	466	0·46
4k	NO_2	H	H	H	NO_2	H	H	431	0·46
4l	H	NO_2	NO_2	H	H	H	H	398	1·20
4m	H	NO_2	H	NO_2	H	H	H	376	0·75
4n	NO_2	H	NO_2	H	NO_2	H	H	427	0·85
4o	NO_2	H	CH_3O	H	H	H	H	470	0·53
4p	NO_2	H	H	H	CH_3O	H	H	445	0·95
4q	CH_3O	H	NO_2	H	H	H	H	415	1·35
4r	H	H	NO_2	H	H	CH_3O	H	402	1·18
4s	H	H	NO_2	H	H	H	CH_3O	403	1·19
4t	H	H	CH_3O	H	H	H	NO_2	395	1·28
4u	CH_3O	H	NO_2	H	CH_3O	H	H	430	1·31
4v	CH_3O	H	NO_2	H	H	H	CH_3O	419	1·37
4w	CH_3O	H	NO_2	H	H	H	NO_2	419	1·33
4x	NO_2	H	CH_3O	H	H	H	NO_2	470	0·53
4y	H	H	CH_3O	H	H	H	CH_3O	389	1·27
4z	NO_2	H	CH_3O	H	H	H	CH_3O	462	0·74

Using the optimised parameters, PPP molecular orbital calculations were carried out on an extensive range of polysubstituted monoazoacetoacetanilides and calculated λ_{max} and oscillator strength values for those compounds are shown in Table 8. In general, the results confirm that the range of colours available from this series of compounds, at least using combinations of electron-withdrawing and -releasing substituents, is fairly restricted. The method predicts that derivatives containing an *o*-nitro substituent in the diazo component ring will generally absorb at longest wavelengths, although it has been pointed out earlier in this section that this particular substituent is likely to give the least accurate prediction of λ_{max}, probably because of intramolecular hydrogen bonding. The *o*-nitro derivatives are also predicted to give the lowest absorption intensities. The highest oscillator strengths are predicted for derivatives containing a *p*-nitro group in the diazo-component ring. Two of the compounds in Table 8 were selected for synthesis to test the success of the predictions. Compound **4o**, (C.I. 11690), for which a relatively high λ_{max} (470 nm) was predicted, was in fact found to be the most bathochromic of the series of products reported in this paper. The experimental λ_{max} for the compound in DMF (428 nm) is somewhat lower than that predicted, presumably because of the presence of the *o*-nitro group. Compound **4s**, selected as an example of a derivative with an electron-withdrawing group in one ring and an electron-releasing group in the other, gave a λ_{max} in DMF of 398 nm, in good agreement with the calculated value (403 nm).

3 CONCLUSION

The λ_{max} values calculated by the PPP molecular orbital method using the generalised set of parameters approach refined by parameter optimisation correlate well with the experimental λ_{max} values for the principal absorption band in the solution UV/visible spectra of a series of monoazoacetoacetanilide pigments which exist exclusively in the ketohydrazone form. The colours of the pigments are restricted to the yellow shade range in solution. There is, in addition, reasonable agreement qualitatively between the experimental molar extinction coefficients and the calculated oscillator strengths. The highest molar extinction coefficients are obtained when the diazo-component ring contains a *p*-nitro substituent.

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 5K min^{-1} and a flowing nitrogen atmosphere. UV/visible spectra were recorded on a Pye–Unicam SP8-200 spectrophotometer interfaced with an Apple microcomputer. First and second derivatives of the spectra were obtained using the Savitsky–Golay method[26] calculated over 15 data points at 1 nm intervals.

4.2 Starting materials

The primary aromatic amines used as diazo components were commercial samples. The acetoacetanilides used as coupling components were commercial samples or were prepared by reaction of the appropriate primary aromatic amine with diketene according to literature procedures.[27] All starting materials were purified by recrystallisation before use.

4.3 Synthesis of the monoazoacetoacetanilides

The amines (0·2 mol) were diazotised in dilute aqueous hydrochloric acid using well-established literature procedures[28] with due attention to keeping the temperature in the range 0–5°C, to maintaining a slight excess of nitrous acid during the diazotisation procedure (starch/KI test) and to destroying any residual excess with sulphamic acid just prior to coupling. The diazonium salt solutions were decolourised using activated charcoal. The acetoacetanilide (0·23 mol) was dissolved in aqueous 5M-sodium hydroxide (45 ml) with stirring and reprecipitated by the dropwise addition of 12% aqueous acetic acid (145 ml). Sodium acetate (23·9 g) was added and the volume made up to 700 ml with water. The diazonium salt solution was pumped into the stirred slurry under the surface of the liquid at such a rate that excess diazonium salt (spot test with alkaline H-Acid solution) was never observed. When coupling was complete, the slurry was heated to the boil and the pigment filtered, washed salt-free with water and freeze-dried. Most of the pigments were purified by recrystallisation from an appropriate solvent (see Table 1). Pigments **2c** and **2d** were purified by chromatography on a column of alumina using as eluants dichloromethane for **2c** and chloroform for **2d**, followed by recrystallisation. Of the pigments prepared, **2c**, **2i** and **4s** were new compounds and the following analytical data were obtained:

2c Found: C, 66·0; H, 5·6; N, 13·6%.
$C_{17}H_{17}N_3O_3$ requires C, 65·6; H, 5·5; N, 13·5%.

2i Found: C, 59·4; H, 4·4; N, 17·2%.
$C_{16}H_{14}N_4O_4$ requires C, 58·9; H, 4·3; N, 17·2%.

4s Found: C, 57·3; H, 4·5; N, 15·6%.
$C_{17}H_{16}N_4O_5$ requires C, 57·3; H, 4·5; N, 15·7%.

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