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Spectrophotometric Investigation and PPP-MO Calculations of Some Phenylazophthalimide Dyes

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ABSTRACT

Spectrophotometric investigations of phthalimide dyes in different solvents have been carried out. The PPP-MO procedure has been used to calculate the anticipated absorption spectra in the visible range as well as the fluorescence absorption maxima of the dyes. On this basis, and employing relationships' between Stokes' shift and the half-bandwidths, the expected intensity of the color has been calculated. Modified parameters for the PPP-MO calculations for the phenylazophthalimide system are given.

1 INTRODUCTION

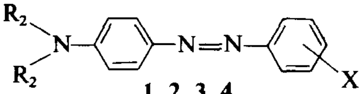
The advantages resulting from the presence of sulfonamide or amide groups in dye molecules have been described in a number of publications.[1–3] Among disperse azo dyes and pigments, dyes containing heterocyclic systems deserve special attention, while dyes with cyclic amide systems[4,5] have been shown to be particularly advantageous. They contain a —CONH— group, which imparts good thermal stability to the dyes. This property results from the ability to self-associate by means of intermolecular hydrogen bonds.[6] Some properties of azo dyes based on phthalimide and naphthalimide (**I**, **II**) derivatives have been described in previous papers.[7–9]

The relationship between structure and color has not yet been developed in detail for these phthalimide derivatives.

In general, the relationship between the color and structure of azo dyes[10] is dependent on the polarization of the molecule, this being the result of the

TABLE 1

UV–Vis Spectroscopic Data for Dyes 1–4



1, 2, 3, 4

X^a	$R_2 = CH_3$					$R_2 = C_2H_5$				
	Dye	λ_{max}^{exp}	S^b	$\lambda_{max}^{calc\,c}$	$\Delta\lambda_{1/2}{}^d(\Delta\nu_{1/2})$	*Dye*	λ_{max}^{exp}	S^b	$\lambda_{max}^{calc\,c}$	$\Delta\lambda_{1/2}{}^d(\Delta\nu_{1/2})$
11-COR	**1a′**		33 (1·75)	417 (+6)		**1a**		29 (1·48)	429 (+7)	
11-CONH$_2$	**1b′**	437	33 (1·80)	412 (−2)	99 (5·12)	**1b**	453	30 (1·57)	423 (−2)	95 (4·72)
11-CONHMe	**1c′**	439	33 (1·77)	415 (+1)	99 (5·20)	**1c**	451	31 (1·59)	426 (+2)	100 (4·96)
11-CONMe$_2$	**1d′**	433	33 (1·82)	410 (−3)	97 (5·12)	**1d**	445	31 (1·64)	420 (−3)	98 (5·04)
10-COR	**2a′**		29 (1·69)	400 (−3)		**2a**		25 (1·39)	411 (−3)	
10-CONH$_2$	**2b′**	425	29 (1·70)	399 (−1)	90 (4·96)	**2b**	436	27 (1·51)	409 (−1)	94 (4·96)
10-CONHMe	**2c′**	427	30 (1·76)	398 (−1)	95 (5·76)	**2c**	436	27 (1·52)	408 (−2)	90 (4·72)
10-CONMe$_2$	**2d′**	428	30 (1·76)	398 (−1)	93 (5·04)	**2d**	436	30 (1·77)	397 (−12)	93 (4·88)
9-COR	**3a′**		32 (1·70)	418 (+1)		**3a**		29 (1·40)	441 (+11)	
9-CONH$_2$	**3b′**	434	33 (1·82)	409 (+14)		**3b**	436	29 (1·54)	420 (−3)	
9-CONMe$_2$	**3d′**	437	30 (1·64)	413 (+22)		**3d**	437	28 (1·60)	405 (−14)	97 (4·88)
H	**4a′**^{e}	403	30 (1·76)	398	88 (6·00)	**4a**	413	27 (1·52)	408	85 (5·00)
		411^f			89 (5·24)		420^f			109 (5·04)
		421^g (394^h)			118 (7·04)		430^g (386^h)			118 (6·72)
11-Cl	**4b′**	415	29 (1·71)	398	83 (5·04)	**4b**	422	25 (1·41)	409	89 (5·20)
		433^f			95 (5·24)		433^f			95 (5·00)
		436^g (404^h)			118 (6·56)		451^g (406^h)			115 (6·20)
11-NO$_2$	**4c′**	454	30 (1·48)	432	86 (4·21)	**4c**	465	29 (1·36)	448	88 (4·16)
		488^f			115 (4·88)		496^f			113 (4·84)
		494^g (434^h)			119 (5·12)		504^g (443^h)			115 (4·76)
11-OMe	**4d′**	405	35 (2·01)	400	84 (5·40)	**4d**	413	31 (1·72)	409	83 (5·04)
		412^f			97 (5·60)		418^f			100 (5·48)
		417^g (388^h)			114 (6·52)		430^g (368^h)			118 (6·08)

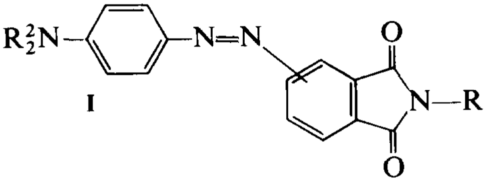
[a] Substituent (R = H, CH$_3$ ...).

[b] Calculated Stokes' shift in nm (and 10^{-3} cm^{-1}).

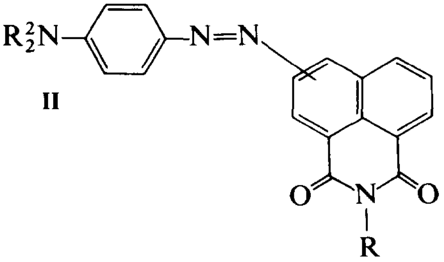
[c] Values calculated using standard parameters (differences of λ_{max} calculated using corrected parameters).

[d] Half bandwidth in nm (and 10^{-3} cm^{-1}).

[e] Absorption in cyclohexane (Chx), [f] MeOH, [g] in DMF and [h] in DMF + 2 × 10^{-5} mol dm^{-3} HCl.



I



II

$R^2 = Me, Et$
$R = H, Me$

interaction between electron-acceptor and donor groups at apposite ends of the conjugated bond system. Hammett σ-values of substituents[3,7,9,11] can act as a measure of this polarization and many authors have shown a good correlation between electronic absorption data and Hammett σ-values for a variety of dyes.[12-15] Such relationships are observed in dyes having one donor and one acceptor substituent. However, when there is more than one donor and one acceptor substituent in the aromatic rings, it is difficult to determine the specific effect of each individual substituent. This is related not only to the mutually competitive effect of the different substituents, but also to the possible occurrence of additional steric effects which can have a considerable influence on the color due to a decrease in the effectiveness of conjugation within the chromophoric system of the molecule.[11] As has been previously found, the presence of two carbonyl groups in the dye molecule has little effect in the case of azo dyes based on naphthalimide derivatives,[12] since both C=O groups are almost equivalent. However, in the case of dyes derived from phthalimide, the color is more dependent on the orientation of the azo group relative to the carbonyl groups.[8]

The object of this present work is to rationalize this problem by investigating the spectra in different solvents of dyes derived from phenylazophthalimide and also by calculating their electron structural parameters using the PPP-MO method (see Section 4.1.2).

The effects of substituents on the acid–base properties of phenylazophthalimide derivatives have also been determined by comparing the spectra of these compounds and the spectra of some reference dyes which are derivatives of *N,N*-dialkylaminoazobenzene and phenylazobenzamides (Table 1).

By applying the PPP-MO method for the prediction of color, the anticipated color of the compound and its intensity have also been calculated.

In many previous investigations, dyes have been characterized using λ_{max} values; this parameter does not fully characterize the dye and to ensure a more complete characterization, it is preferable also to know the absorption bandwidth. The possibility of using the PPO-MO method for predicting absorption bandwidths has been reported,[16] based on an analysis of the shift of the expected fluorescence absorption bandwidth (Stokes shift) according to the relationships proposed, for example, by Pestemer.[17]

The basic relationships have been described in a number of papers, in which the PPP-MO method was used for calculating the position of the fluorescence maxima of a number of dyes, as well as the electronic states of the molecules in both the ground state and the excited state.[18-25] The method has recently been used[16] for calculating the absorption bandwidth of a range of dyes and the results obtained were largely in agreement with the experimental data. The method has not been used so far in studies of dyes containing a phthalimide residue and relevant data in this respect are presented in this present paper.

2 EXPERIMENTAL

Dyes **4a–4d**, **4a–4d** were prepared and purified as described previously.[5] The synthesis and some properties of dyes **1**, **2**, **3a–3d**, **3a–3d**, and **5a–5h** have been described previously.[26] Absorption spectra of dyes **1–5** were made on a Spectord UV-VIS (Zeiss-Jena) spectrophotometer using solutions of dyes **1–4** in cyclohexane (Chx), methanol (MeOH) and *N,N*-dimethylformamide (DMF). The spectra of dyes **5a–5h**, due to their low solubility, were determined in the form of saturated solutions in Chx and MeOH, and in *N,N*-dimethylformamide at a concentration of 2×10^{-4}–2×10^{-5} mol dm^{-3}. In acid and basic media, spectra were made following the addition of 1 cm^3 of 96% H_2SO_4 or 2·5 cm^3 of 30% NaOH to the dye solution in methanol. Spectra were also recorded in 50% aq. methanol. All solutions were kept for 24 h in the dark prior to spectra measurement.

3 RESULTS AND DISCUSSION

3.1 Spectral characteristics of dyes

The dyes derived from phenylazo-3- (**5a–5d**) or 4-phthalimide (**5e–5h**), show absorption maxima within the range 436–496 nm (Table 2): the position depends, to varying extents, on the nature of the dialkylamino residue in the

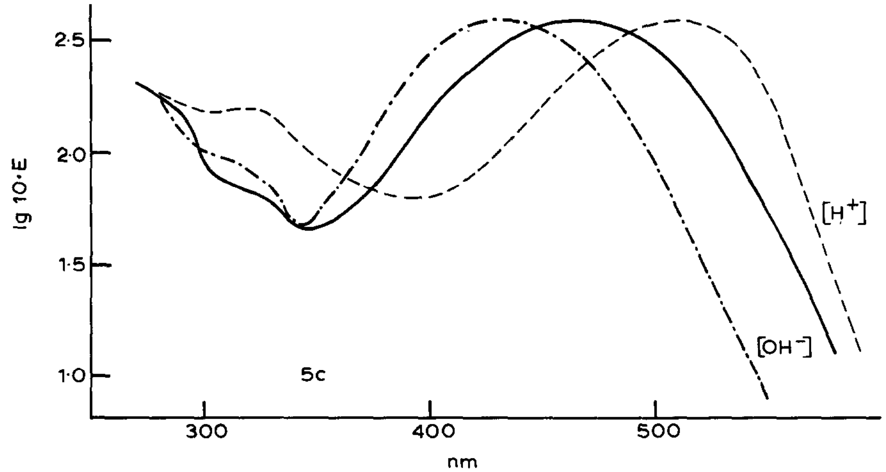


Fig. 1. Spectra of dye **5c** on methanol. $[H^+] = 1{\cdot}8 \times 10^{-2}$ mol/dm^3; $[OH^-] = 2{\cdot}5 \times 10^{-2}$ mol/dm^3.

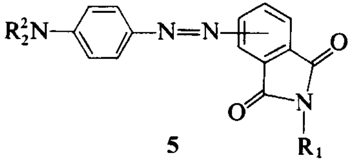
coupling component, on the orientation of the azo group, and on the type of solvent used for the measurement of spectra. Representative spectra of dye **5c** are shown in Fig. 1.

*3.1.1 Spectra of reference dyes derived from aminoazobenzenes (**4**) and phenylazobenzamides (**1–3**)*

The spectral properties of dyes **1–3** derived from phenylazobenzamide have been previously discussed.[26] These data are given in Table 1 to enable comparison to be made with the dyes derived from phenylazophthalimide (**5**). For dyes **4**, spectra were recorded in cyclohexane (Chx), methanol (MeOH) and *N*,*N*-dimethylformamide (DMF). Representative spectra (for **4c**) are shown in Fig. 2. The position of the absorption bands depends mainly on the nature of the *N*,*N*-dialkylamino residue. The alkalinity of the *N*,*N*-diethylamino group is greater than that of the *N*,*N*-dimethylamino group, as is demonstrated by their Taft σ_I- constants, viz. $-0{\cdot}22$ and $-0{\cdot}16$ respectively.[27] The bathochromic shift in λ_{max} (in Chx) ranges from 7 to 11 nm for dyes **4a–4d**; when MeOH and DMF are used as solvents, λ_{max} is shifted to longer wavelength because of solvation effects, and, at the same time, the absorption bands broadened.

These differences result in the correlations of the function $\lambda_{max}^{exp} = \lambda_{max}^{calc}$ being different for the *N*,*N*-dialkylamino residue, with values of $r = 0{\cdot}936$ (for $—NMe_2$) and $r = 0{\cdot}942$ (for $—NEt_2$) in DMF. Values of $\lambda_{max}$for dyes **1–5** were used for these calculations. It was also concluded that considerations should be based mainly on spectra in DMF and Chx, since MeOH can result in ambiguous spectral effects due to the formation of different intermolecular hydrogen bonds.[28,29]

TABLE 2
UV-Vis Spectroscopic Data for Phenylazophthalimide Dyes (**5**)



5

Dye	*Isomer*	R_2	R_4	$\lambda_{max}^{exp\ a}$	S^b	$\lambda_{max}^{calc\ c}$	$\Delta\lambda_{1/2}{}^d(\Delta\nu_{1/2})$	σ^e	*MeOH/H⁺*			*MeOH/OH⁻*		*50% MeOH*	
									$\lambda_{max}{}^{fx}$ (log *10E*)		$\Delta\lambda_1{}^g$	$\lambda_{max}{}^y$ (log *10E*)	$\Delta\lambda_2{}^g$	$\lambda_{max}{}^z$	$\Delta\lambda_3{}^g$
5a	3-	Me	H	438 454 (2·46)^j 461^k	35 (1·59)	430 (+30)	85 (4·48) 107 (5·32) 111 (5·20)	0·38	311 (1·84)	506 (2·55)	52	430 (2 43)	−24	474	20
5b	3-	Me	Me	436 456 (3·12)^j 460^k	34 (1·58)	426 (+27)	85 (4·64) 112 (5·57) 103 (5·44)	0·41	309 (2·70)	506 (3·18)	50	421 (3·10)	−35	479	23
5c	3-	Et	H	447 466 (2·60)^j 474^k	36 (1·51)	445 (+34)	80 (4·12) 107 (5·10) 107 (4·88)	0·50	315 (2·09)	506 (2·38)	40	439 (2·61)	−27	488	22

5d	3-	Et	Me	472 468 (3·08)[j] 472[k]	34 (1·46)	442 (+32)	84 (4·36) 110 (5·21) 106 (4·96)	0·60	315 (2·70)	510 (3·09)	42	431 (3·08)	−37	490	22
5e	4-	Me	H	439 466 (1·98)[j] 481[k]	31 (1·38)	441 (+24)	97 (5·16) 113 (5·41) 117 (5·28)	0·50	322 (1·41)	517 (2·14)	51	439 (1·96)	−27	485	19
5f	4-	Me	Me	442 473 (2·26)[j] 485[k]	32 (1·44)	439 (+23)	89 (4·68) 111 (5·18) 111 (4·96)	0·53	328 (1·60)	512 (2·11)	39	427 (2·26)	−46	494	21
5g	4-	Et	H	454 481 (2·42)[j] 496[k]	30 (1·26)	455 (+26)	86 (4·24) 109 (4·97) 108 (4·64)	0·67	321 (2·03)	521 (2·44)	40	456 (2·39)	−25	498	17
5h	4-	Et	Me	452 488 (2·39)[j] 494[k]	30 (1·28)	453 (+25)	87 (4·32) 108 (4·81) 100 (4·32)	0·75	327 (2·03)	519 (2·40)	31	442 (2·38)	−46	506	18

[a] Absorption in CHx (in saturated solution), [j] in MeOHC log 10E) (*in saturated solution*), *and* [k] in DMF (data from Ref. 26).

[b] Calculated Stokes' shift in nm (and 10^{-3} cm^{-1}).

[c] Values calculated using modified parameters (differences of λ_{max} calculated using standard parameters[16]).

[d] Halfwidth in nm (and 10^{-3} cm^{-1}).

[e] Calculated Hammett σ-constants.

[f] Absorption in MeOH/H^+.

[g] $(\Delta\lambda_1, \Delta\lambda_2, \Delta\lambda_3) = (\lambda_{max}^{x}, \lambda_{max}^{y}, \lambda_{max}^{z}) - \lambda_{max}^{exp}$, respectively.

[h] Absorption in MeO/OH^-.

[i] Absorption in 50% MeOH/H_2O.

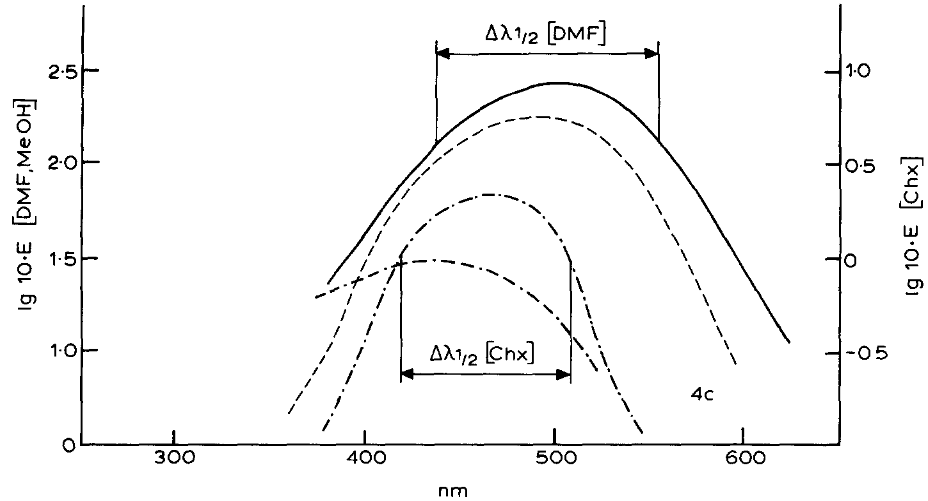


Fig. 2. Spectra of dye **4c** in cyclohexane (–·– –), methanol (– – – –), DMF (——) and DMF/H^+ (–– ––) solution.

The broadest absorption maxima are shown in dye solutions in DMF, and the strongest hyperchromic effect in their solutions in Chx, since there is no interaction with the solvent in this medium.

3.1.2 Spectra of dyes derived from phenylazophthalimides, 5

3.1.2.1 Spectra in cyclohexane (Chx). The spectra of the reference dyes **4** and phthalimide dyes **5** were recorded in Chx and in view of their low solubility, measurements were made only in the form of saturated solutions. Since there is no interaction between the solvent and the dye molecule, the effect of specific functional groups on the color of dyes can be assessed. By comparing the spectra of dyes **5** and the reference dyes **4**, Hammett σ-values of the cyclic phthalimide system were calculated.

The absorption maxima of dyes **5a**–**5h** are shifted bathochromically in relation to dyes **4** due to the presence of the electron acceptor phthalimide residue. The phthalimide residue, however, is a weaker acceptor substituent than the —NO_2 group in the 11-position, as is indicated by comparison of the Hammett σ-values of the nitro group (0·78) and the calculated values for the different phthalimides (0·38–0·75; Table 2).

The calculated σ-values are higher for all the *N*-methylimides relative to analogous imides and also show large differences between isomeric dyes in which the azo group is substituted at the 3- or 4-positions. The carbonyl groups in these dyes are either *meta* and *para* (in the 4-isomers) or *ortho* and *meta* (in the 3-isomers) to the azo group and only one of them is directly conjugated to the azo group.

In the 4-isomer, the molecule is planar and hence conjugation is maximized, but in the 3-isomer there are steric interactions between the nitrogen atom N(6) of the azo bond and the adjacent carbonyl group C(12)=O(13). This results in a hypsochromic shift in $\lambda_{max}$when comparing isomers **5a**–**5d** in relation to **5e**–**5h**. These observations are confirmed by the calculations made by the PPP-MO method which are discussed later. Because of the steric hindrance, the molecules of derivatives of 3-phenylazôphthalimide (**5a**–**5d**) are twisted relative to the N(7)–C(8) bond, and, based on crystallographic studies,[30] the angle of twist is 32·8°.

3.1.2.2 Spectra in methanol and N,N-*dimethylformamide.* In dyes **5a**–**5d**, the effect of the change of the solvent from Chx to MeOH or DMF manifests itself in a shift of absorption by 23–27 nm for the 3-isomers or 42–43 nm for the 4-isomers. As in the reference compounds **4**, this is additionally accompanied by a distinct broadening of the absorption bands (cf. Section 1.1).

The lower bathochromic effect in dyes **5a**–**5d** indicates that solvent interaction occurs at the carbonyl groups participating in the conjugation, i.e. those in the *ortho* and *para* positions. This is particularly significant in the 3-isomers, in which the steric factors hinder both solvation and conjugation. In our considerations, the carbonyl group in the *meta* position, which can affect the spectrum only through the inductive effect and which should have a constant effect for both isomers, was neglected (see Section 4.2).

The solvation in DMF can be demonstrated from considerations of the spectra of the reference dyes **4** in the presence of small amounts of HCl (2×10^{-5} mol dm^{-3}) comparable with the dye concentration. An addition of this amount of acid does not result in a bathochromic effect, as is generally observed,[31,32] but in a hypsochromic effect (Table 1, **4a**–**4d**, **4a′**–**4d′**). Under these conditions, protonation of the strongly nucleophilic centre, i.e. the *N*,*N*-dialkylamino residue, probably occurs, thus removing its conjugative effect and rendering solvation by means of DMF difficult. The relationships between absorption maximum in DMF solution and the Hammett σ-value are linear with correlation coefficients, r_1 and r_2, of 0·998 (NEt_2 derivatives) and 0·986 (NMe_2 derivatives), respectively.

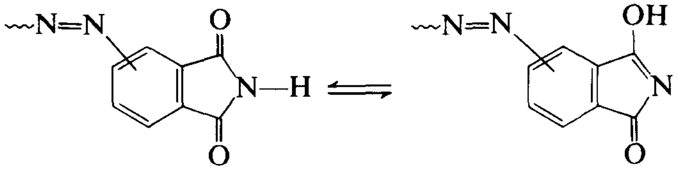
The observed spectral indicate that DMF solvates mainly the *N*,*N*-dialkylamino groups as electron-donor centres, and consequently this solvent can be used instead of Chx for analyses of the visible spectrum, especially for compounds having the same nucleophilic centre (i.e. *N*,*N*-dialkylamino end-group).

The nature of the solvent also has a distinct effect on the absorption bandwidths of the dyes. In contrast to dyes **4**, for which differences in $\Delta\lambda_{1/2}$ in MeOH and Chx are small, in the phenylazophthalimides **5a**–**5h** clear differences are apparent between Chx, on the one hand, and MeOH and

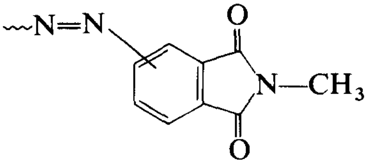
DMF on the other. This tends to confirm the specific role played by the phthalimide residue, and probably implies that its solvation has a strong influence on the occurrence and stabilization of polar forms over a different length of the conjugated chain, resulting in broadening of the absorption bands.

Values of λ_{max} of dyes containing an imide (—NH) and *N*-alkylamide (—NMe) group do not allow the effect of the —NMe residue on the spectrum to be exactly determined. Differences are relatively small and can be of random character but, in MeOH, particularly with derivatives of 4-phenylazophthalimide, a small bathochromic effect (approx. 7 nm) for the —NMe derivatives in relation to the —NH derivatives is apparent. The latter derivatives can also exist in the form of a mixture of tautomeric keto and enol forms, because of the acidic character of the imide hydrogen atom ($pK_a = 9{\cdot}9$[33,34]), whereas the *N*-methyl derivatives can only exist in the ketone form.

Imide: keto–enol tautomerism



N-Methylimide



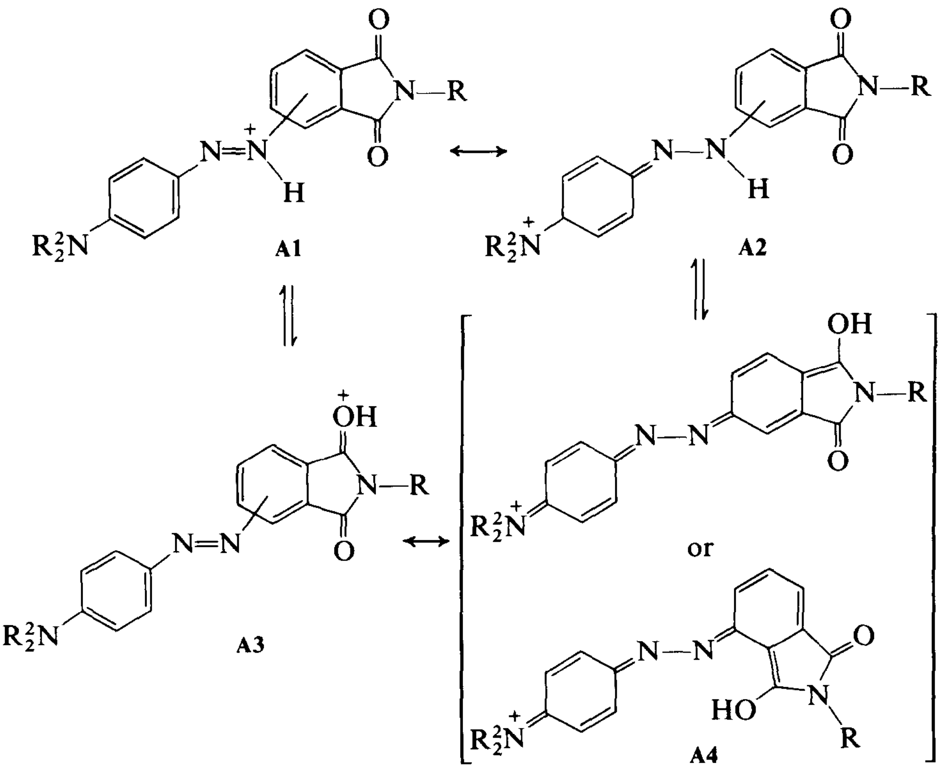
In MeOH, dyes **4** can undergo solvation both at the azo group (leading to a bathochromic and hypochromic effect) and at the *N*,*N*-dialkylamino residue[28,31,32] (leading to a hypsochromic and hyperchromic effect). The phenylazophthalimide dyes **5** can behave in a similar way, but can also undergo additional solvation at the imide residue. The diversity of these effects and especially the fact of their simultaneous occurrence results in correlations between calculated and determined λ_{max} to be different for different solvents. In contract to the effect of MeOH, DMF complexes only with electron-donor centres (see Section 3,1,2,2), and correlation coefficients of the function λ_{max}^{exp} (DMF, ChX) = $f(\lambda_{max}^{calc})$ (Tables 1, 2) for dyes **4** and **5** are very similar; they are represented in eqns (1) and (2):

$$\text{DMF: } r = 0{\cdot}938 \qquad \lambda_{max}^{exp} = 100 + 0{\cdot}71 \times \lambda_{max}^{calc} \tag{1}$$

$$\text{Chx: } r = 0{\cdot}943 \qquad \lambda_{max}^{exp} = 26 + 1{\cdot}05 \times \lambda_{max}^{calc} \tag{2}$$

3.1.2.3 Spectra in MeOH of different pH. In view of the presence of three proton-acceptor centres in the phenylazophthalimide derivatives **5**, it was expected that their behavior in solutions of different pH would be relatable to the behavior of typical azo dyes^{35} which usually undergo protonation on the azo bond in acidic solutions. Using also data from the spectra of dyes **5** in 50% aq. MeOH, i.e. in a solvent stabilizing the hydrazone form of the dyes, some insight into possible tautomerism in the phenylazophthalimide dyes was anticipated. The results obtained are presented in Table 2. Dye spectra in a neutral MeOH solution have been discussed in Section 3.1.2.2.

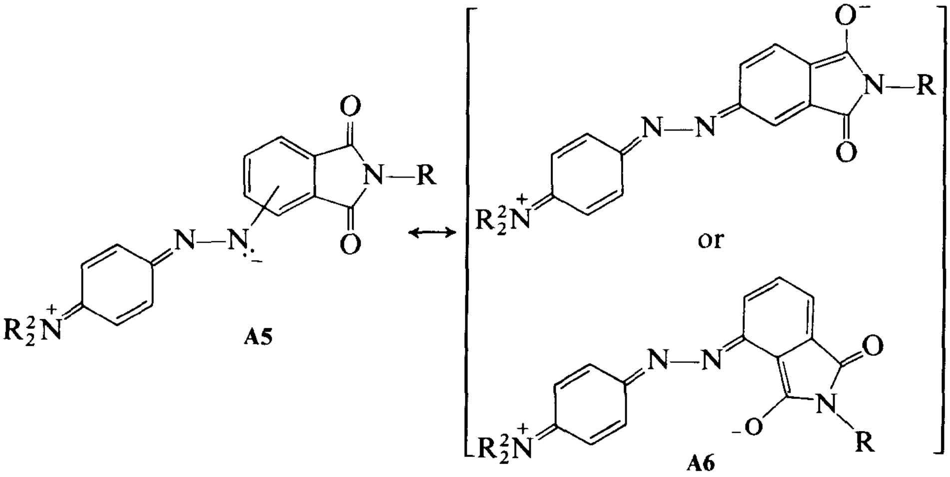
In acidic medium additional absorption bands occur in the range 506–519 nm and weak bands over the range 309–327 nm (Fig. 1). These are probably, as in other azo dyes$^{7,8,36-40}$ the result of protonation on the β-nitrogen atom of the azo group.



A probable structure of the protonated form can be postulated based on considerations of the changes in the spectra over the visible range, and the influence of the structural changes in the dye molecule, viz. the orientation of the azo residue (3- or 4-), the type of the *N*,*N*-dialklamino residue (—NMe$_2$ or —NEt$_2$) and the type of the substituent in the imide residue (—NH, or —NMe).

Investigations were made out using variable acid concentrations in the solvent. In these cases, no isosbestic point was observed and the absorption was shifted bathochromically, with lower intensity. This demonstrates the contribution of several different factors to the spectrum, thus hindering adequate interpretation of the results. Structure **A4** is the most probable of the forms suggested since, in this case, interaction of the cyclic imide system and the dye chromophore system occurs. A slight bathochromic effect in the 4-isomer in relation to the 3-isomer reveals also the existence of steric hindrance in the latter. A similar bathochromic effect is produced by changes in the *N*,*N*-dialkylamino group and the influence of the substituent on the heterocyclic nitrogen atom of the imide residue (0–5 nm) can be regarded as incidental.

Spectra in methanol solution with addition of NaOH or in 50% aq. MeOH provide further evidence concerning the structure of the compounds under discussion. According to published data, in aqueous alcoholic solutions a number of dyes occur either in the form of a mixture or show the predominance of either the azo or hydrazone forms.[41,42] With no other possibilities of isomerization, this should manifest itself in the occurrence of an isosbestic point in solutions of varied alcohol concentration. The spectra of dyes **5a**–**5h** in 50% aq. MeOH showed, in all cases, bathochromic shifts relative to the spectra in pure MeOH. No isosbestic point was observed resulting from changes in the concentration of dyes with respect to the varying alcohol content of the solution. The bathochromic shift of 17–23 nm in 50% aq. MeOH is an indication of the occurrence of the more polar form, typified by **A6.**



A5

A6

In alkaline solution, on the other hand, a hypsochromic effect of 25–46 nm was observed, the higher values 35–46 nm being for dyes (**5b**, **5d**, **5f**, **5h**) containing the *N*-methylimide group, compared with 25–27 nm in the case of dyes (**5a**, **5c**, **5e**, **5g**) with —NH groups. Such an effect is characteristic of compounds more strongly solvated in their ground state than in the excited state. This solvation reduces the effective positive charge on forms **A5** ↔ **A6**, reducing the dipole moment of the molecule and causing a hypsochromic effect.

4 CALCULATIONS OF SPECTRA BY THE PPP-MO METHOD

The PPP-MO method was used for the compounds **1–4** (Table 1), by applying the basic parameters quoted in the literature.[16,41–44] The bandwidth of these dyes was calculated as proposed by Pestemer[17] and as employed by previous authors.[16] The standard set of parameters was also used for the phenylazobenzamide dyes (**1–3**) and the phenylazo-3- and -4-phthalimide (**5**) derivatives. The results of the calculations are given in Tables 1 and 2, which also show the results of calculations performed using modified parameters, and with which a better correlation with the experimental data was obtained.

The use of the PPP-MO method for the calculation of the half-bandwidth resolves itself into calculating a theoretical absorption band of the fluorescence of the dye. This is done after the input data have been modified, with regard to the changes resulting from the absorption of light and after the molecule has passed to the excited state. Re-emission of radiation takes place always over the longer-wavelength range; hence the fluorescence band should be shifted bathochromically in relation to the absorption band. As has been found by many authors,[16,18–21,23,24] in the PPP-MO method it is sufficient to take into account only the changes in the length of bonds and the values of resonance integrals β, according to the relationships proposed above.[18–25] Changes in the remaining parameters taken into account in the calculations, such as ionization potential and electron affinity, have no significant effect on the value of the position of the fluorescence maximum. The calculated value of the Stokes shift allows the determination of the half-bandwidth, and consequently the color purity of the dyes according to the equation ($\Delta\lambda = 2{\cdot}5S$) proposed by Pestemer[17] and used by Cheng *et al.*[16] In Pestemer's calculations, the value of the factor of proportionality varied between 1·91 and 3·67 (relative error, −23·2% to +46·8%). The relationship for theoretical spectra has also been given[11] in the form:

$$\Delta\nu_{1/2} = 0{\cdot}727 + 1{\cdot}937 \times S$$

and a correlation coefficient $r = 0{\cdot}945$ obtained. It is more advantageous to use $\Delta\nu_{1/2}[\mathrm{cm}^{-1}]$ than $\Delta\lambda_{1/2}[\mathrm{nm}]$.

The method is of a semi-empirical character and allows an approximate prediction of the dye color intensity. Such calculations can be made even for dyes which do not exhibit fluorescence and for which the value of the Stokes shift cannot be measured.

4.1 Calculations of electron structures of phenylazophthalimide dyes and the half-band width

4.1.1 Calculations of parameters for dyes 1–4

Applying the standard set of parameters,[16,17] calculations were performed for the phenylazobenzeamide dyes **1–3** for which basic spectrophotometric data have been published previously.[26] Satisfactory agreement between the calculated and experimental data was obtained. The differences in the values of the calculated and experimental λ_{max} result from the effect of the solvent, especially of DMF, on the dye spectrum (Tables 1 and 2). This solvent shifts the absorption bathochromically and broadens the absorption bands. In extreme cases the differences quoted for dyes **4** are of the order of 39–42 nm (dyes **4c** and **4c′**). The results obtained confirm the lack of interaction of substituents in the *meta* position (dyes **2a–2d** and **2a′–2d′**), the spectrum being identical to the calculated value for dye **4a**. The *ortho* and *para* show a slight bathochromic effect, and the supposition that the substituent in the *ortho* position to the azo bond is non-coplanar cannot be confirmed.

4.1.2 Calculations of spectra of dyes derived from phenylazophthalimide

Calculations for dyes derived from phenylazophthalimide were initially made based on standard parameters,[16,17] and results inconsistent with the experimental values determined in Chx were obtained. They were underrated by about 23–34 nm. This led to further considerations with respect to the character of the phthalimide system and its effect on the spectrum. In this connection, the following modified parameters were used for the calculations:

	VSIP*	γ_y (A_y)
C=O	18·10	14·95 (3·15)
N—CH$_3$	21·00	11·00 (10·00)
N—H	24·65	14·55 (10·15)

* Valence State Ionisation Potential.

Values of λ_{max} and $\Delta\lambda_{1/2}$ conforming to those determined in Chx were obtained, especially for the 4-isomers **5e–5h** (Table 2). The differences in the values calculated, based on standard parameters, are shown in parentheses. In calculating data for the 3-isomers (**5a–5h**), the twisting around the N(7)–C(8) bond by an angle of $\theta = 30°$ was additionally taken into account (the angle of twist is 32·8°[30]) and modifying the input parameters for the calculations according to the relationships:[43]

$$\beta = \beta_0 \cos\theta$$

and

$$\gamma_\theta = \gamma_0 \cos^2\theta$$

According to the results of X-ray investigations,[45] the 4-isomer has a flat structure. The values of λ_{max} thus calculated are in agreement with the experimental values determined in Chx according to the relationship:

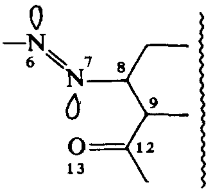
$$\lambda_{max}^{exp} = 1{\cdot}58 \times \lambda_{max}^{calc} - 263$$

with a correlation coefficient $r = 0{\cdot}993$ for dyes **5a**–**5h**. Calculations for the 3-substituted derivatives are additionally complicated by the possibility of the occurrence of these isomers in four different spatial conformations, viz. α-*trans*, α-*cis*, twisted α-*trans* and twisted α-*cis* (Table 3).

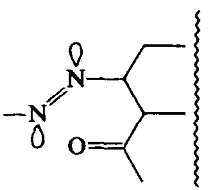
TABLE 3

Influence of Spatial Configuration of Dyes **5a**–**5d** on the Calculated Values of Absorption (nm). (For calculation, the twisting around the N(7)–C(8) bond by an angle of $\theta = 30°$ was taken into account).

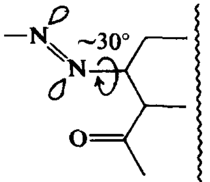
Dye	α-trans[a]	α-cis[b]	*Twisted* α-trans[c]	*Twisted* α-cis[d]
5a	447	452	430	437
5b	444	448	426	432
5c	462	468	445	453
5d	458	463	442	448



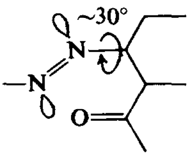
a α-*trans*



b α-cis



c Twisted α-*trans*



d Twisted α-*cis*

Theoretical considerations indicate that the 3-azophthalimide dyes **5a**–**5d** most probably exist in the *α-cis* configuration, which has the deepest color. In this configuration there are no interactions between the carbonyl oxygen atom O(13) and the free electron pair of the nitrogen atom N(6) of the azo bond. It has been found,[30] however, that these dyes in the crystalline state occur in the twisted *α-trans* form, for which calculated values are given in Table 3. They are consistent with the λ_{max} determined in Chx solution (Table 2).

For the observed and calculated values for dyes **5a**–**5h** of

$$\lambda_{max}^{exp}(\mathrm{DMF, Me, Chx}) = f(\lambda_{max}^{calc})$$

based on the standard and modified parameters, correlation parameters between these values were determined:

	DMF	Me	Chx
Standard parameters	0·990	0·952	0·924
Corrected parameters	0·902	0·905	0·993

The results indicate that, for comparison between experimental values and those calculated by the PPO-MO method, and not taking into consideration solvent interactions, correlations in Chx are not satisfactory, but that for similar analysis in DMF the standard parameters used do reflect the effect of this solvent on the electron state of the molecule.

In this case, the differences between experimental and calculated values are much greater than in Chx, being in the region of 31–46 nm (as opposed to 1–10 nm in Chx). This procedure can therefore be recommended for compounds which are sparingly soluble in non-polar solvents, although precise results are not obtained.

The set of modified parameters used gives good correlations only for the phenylazophthalimide derivatives **5a**–**5h**. Attempts to use compounds **1**–**3** (Section 4.1.1) in such calculations yielded results which, in some cases, differed considerably from the values obtained based on the standard parameters, and these differences are given in Table 1. The calculation results have been compared with the spectra made in Chx, with the assumption of the absence of interactions with the solvent. The use of other solvents for measuring the spectra results in additional interactions with the dye molecule and, as a result, the spectrum shape and the position of λ_{max} are changed.

Using the PPP-MO procedure and modified parameters for the molecule in the excited state, it is possible to calculate theoretical values of the fluorescence maxima of the compounds with the test for convergence of 0·002. Only the parameters of bond and resonance integrals undergo modification, according to the relationship suggested.[16,24] The Stokes shifts calculated are given in Tables 1 and 2, and they are proportional to the half-bandwidths in nm or cm^{-1}.

$$\Delta\lambda_{1/2} = 2{\cdot}79 \times S \text{ (error from } -20{\cdot}4\% \text{ to } +27{\cdot}6\%) \quad [\text{nm}]$$

$$\Delta\nu_{1/2} = 3{\cdot}13 \times S \text{ (error from } -14{\cdot}7\% \text{ to } +19{\cdot}4\%) \quad [\text{cm}^{-1}]$$

In the case of the phenylazophthalimide derivatives, these values have a considerable error, the cause of which could be the absence of coplanarity. In view of the semi-empirical nature of the calculation method, its accuracy depends on the correct selection of parameters determined on the basis of the experimental data and improvements in it require further investigations using a large number of other chromophore systems. However, in its present form, the method can be applied for predicting the intensity of color of new chromophores with an accuracy sufficient for most practical purposes.

4.2 Electron densities and bond orders

4.2.1 Dyes derived from phenylazobenzamide (1–3)

The PPP-MO method can also be used to calculate the electron densities and bond orders. In the ground state, in dyes derived from phenylazobenzamide (Table 4—**1**, **2**, **3**), the principal electron-rich sites are carbon atoms *ortho* and *para* to the donor residue, the β-nitrogen atom and, to a lesser extent, the α-nitrogen atom. No distinct effect of the amino group of the amide residue

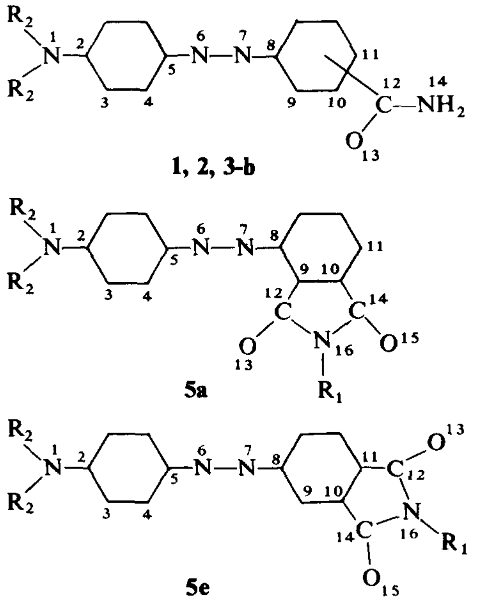


Fig. 3. Numbering of atoms and bonds listed in Table 4.

TABLE 4

Calculated Bond Orders and π-Electron Densities in Ground (Excited) State for Some Benzamide and Phthalimide Dyes (Fig. 3)

Bond	**1b′**	**2b′**	**3b′**	**5a′**	**5e**	*Atom*	**1b′**	**2b′**	**3b′**	**5a**	**5e**
1–2	0·55 (0·63)	0·55 (0·62)	0·55 (0·63)	0·56 (0·67)	0·59 (0·68)	1	1·69 (1·39)	1·69 (1·39)	1·69 (1·40)	1·68 (1·33)	1·68 (1·35)
2–3	0·56 (0·48)	0·55 (0·48)	0·55 (0·48)	0·55 (0·48)	0·53 (0·48)	2	0·98 (0·99)	0·98 (1·00)	0·98 (0·99)	0·95 (0·94)	0·95 (0·95)
3–4	0·71 (0·74)	0·71 (0·74)	0·71 (0·74)	0·72 (0·75)	0·72 (0·75)	3	1·11 (0·99)	1·11 (0·99)	1·11 (0·99)	1·12 (0·98)	1·12 (0·98)
5–6	0·42 (0·45)	0·43 (0·47)	0·43 (0·46)	0·44 (0·43)	0·45 (0·44)	4	0·95 (1·00)	0·95 (1·01)	0·96 (1·01)	0·95 (0·95)	0·95 (0·97)
6–7	0·85 (0·63)	0·82 (0·56)	0·82 (0·60)	0·83 (0·81)	0·81 (0·76)	6	1·07 (1·33)	1·08 (1·35)	1·07 (1·33)	1·05 (1·12)	1·06 (1·18)
7–8	0·32 (0·46)	0·37 (0·48)	0·37 (0·50)	0·33 (0·37)	0·38 (0·44)	7	1·12 (1·24)	1·14 (1·29)	1·13 (1·26)	1·13 (1·08)	1·08 (1·11)
8–9	0·60 (0·52)	0·62 (0·56)	0·61 (0·54)	0·62 (0·54)	0·59 (0·60)	8	0·96 (0·98)	0·97 (0·98)	0·96 (0·98)	0·92 (0·96)	0·95 (0·99)
9–10	0·64 (0·63)	0·65 (0·66)	0·69 (0·72)	0·59 (0·52)	0·67 (0·65)	9	1·00 (1·05)	1·00 (1·04)	1·00 (1·03)	1·02 (1·12)	0·94 (0·92)
10–11	0·67 (0·68)	0·63 (0·61)	0·62 (0·58)	0·65 (0·62)	0·58 (0·50)	10	1·01 (1·01)	1·01 (1·01)	1·02 (1·02)	1·03 (1·09)	1·03 (1·08)
n^*–12[a]	0·32 (0·37)	0·30 (0·30)	0·32 (0·36)			11	1·05 (1·01)	1·01 (0·97)	1·05 (1·00)	0·94 (0·93)	1·02 (1·10)
12–13	0·63 (0·60)	0·63 (0·63)	0·63 (0·60)	0·72 (0·57)	0·71 (0·59)	12	0·88 (0·89)	0·88 (0·88)	0·89 (0·89)	0·71 (0·85)	0·72 (0·84)
14–15				0·71 (0·58)	0·72 (0·62)	13	1·38 (1·39)	1·39 (1·39)	1·39 (1·39)	1·53 (1·63)	1·53 (1·62)
12–16	0·63 (0·60)	0·64 (0·64)	0·63 (0·61)	0·48 (0·48)	0·47 (0·47)	14	1·77 (1·77)	1·75 (1·75)	1·76 (1·76)	0·72 (0·88)	0·72 (0·82)
9(11[b])–12				0·32 (0·45)	0·32 (0·44)[b]	15				1·50 (1·63)	1·51 (1·59)
10–14				0·31 (0·42)	0·31 (0·40)	16				1·67 (1·67)	1·67 (1·67)

[a] $n^* = 9$(*ortho*), 10(*meta*), 11(*para*).

[b] 11–12 bond in dye **5e**.

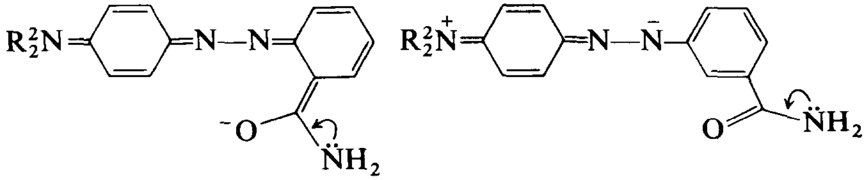
on the electron density, either in the ground or excited state, is observed. Electron excitation causes conjugation of the electron pair of the nitrogen atom of the —NR_2(1) group and the formation of a quinonoid-type structure. This manifests itself in changes in the electron density of the azo group, e.g. on the α-nitrogen atom [N(6)]. The bond order N(6)–N(7) for dyes **1b**′, **2b**′, **3b**′ decreases in the order:

2b′ (0·26) > **3b**′ (0·22) > **1b**′ (0·21)

but that for N(7)–C(8) is in the reverse order, viz.

1b′ (0·14) > **3b**′ (0·13) > **2b**′ (0·11)

The difference between the bond order in the excited state and that in the ground state is given in parentheses. This shows that the strongest conjugation, in accord with predictions, occurs for *para*-isomers of **1**. The second substituent taking part in the conjugation is the C=O carbonyl group which is in the *meta* postion, but unlike the *para* and *ortho* isomers, this does not change its bond state and electron density. In these dyes (**1**–**3**) the character of the double bond between the carbon atom and the oxygen atom is modified, to give a partial single bond, which contributes to the polarization in the excited state:



This is confirmed by the experimental and calculated λ_{max} values, which are lowest for the *meta* derivatives (**2**).

4.2.2 Dyes derived from phenylazophthalimide

In the ground state, dyes derived from phenyl azophthalimide (**5**) (Table 4) have a similar distribution of electrons to the dyes derived from phenylazobenzenamide (**1**, **2**, **3**), with slightly different values, particularly in the phenylazo system. Significant differences occur in the electron-acceptor carbonyl residues. In the phthalimide dyes **5a** and **5e**, these groups are much more strongly polarized than in the benzamide analogues **1b**′, **2b**′, **3b**′; there is a positive charge [+0·28 and 0·29 on the carbon atoms C(12,14)], but an excess negative charge [−0·50 and 0·51] on the oxygen atoms O(13,15). The polarization of the carbonyl bonds is increased in the excited state and the bond orders are changed. As with the amide group NH_2(14) (Fig. 3) in dyes **1b**′, **2b**′, **3b**′, the imide group NH(16) in dyes **5a** and **5e** does not participate significantly in the conjugation; the electron density on it is lower due to the presence of the two adjacent carbonyl groups, and the C(12)–N(16) bond is longer.

The dependence of bond orders in the aromatic system on the orientation of the carbonyl groups in the ring is observed. Bonds C(9)–C(10) (**5a**, **3**-substituted isomer) and C(10)–C(11) (**5e**, 4-substituted isomer) are longer than the adjacent, typical C–C bonds in the phenyl ring, whilst in the excited state they are further lengthened. In the excited state, there is additional distinct polarization of the C=O bonds, together with bond lengthening, in the *ortho*, *meta* and *para* positions to the azo bond. This indicates that the C=O group in the *meta* position does participate in the conjugation; it does so not by direct interaction with the N=N azo group or the *N*,*N*-dialkylamino group, but with the adjacent carbonyl group. The absence of such changes in the benzamide derivatives confirms this supposition (Table 4, bonds *n*–12).

In isomer **5a**, polarization of the C(10)–O(14) group is even greater than that of C(9)–O(12), which can also be caused by the absence of molecular coplanarity (Section 4.1.2). Polarization of both groups is greater than for isomer **5e** in which the C=O bond has greater double bond character. The hindered conjugation, however, results in a hypsochromic effect for these derivatives (**5a**–**5d**). The results of the calculations offer an explanation of the cause of the occurrence of significant differences in the spectra of phenylazobenzamide (**1**–**3**) and phenylazophthalimide (**5**) dyes.

5 CONCLUSION

Azo dyes derived from 3- and 4-aminophthalimide have orange to red hues, depending on the substituent type at the imide nitrogen atom and the *N*,*N*-dialkylamino residue in the coupling component. In neutral solutions and in solutions of different pH values these dyes exhibit solvatochromic and halochromic color effects. It has been found that polar solvents, due to the formation of solvated structures, mainly on the electron-donor centre, cause broadening of the absorption bands and a dulling of the hue. Protonation of the β-nitrogen atom of the azo group results in a bathochromic shift of about 30–45 nm, for both 3- and 4-aminophthalimide derivatives.

It has also been found that, in 50% aq. methanol, phenylazophthalimides occur essentially in the hydrazone forms, with absorption maxima bathochromically shifted by 17–23 nm. These forms are stabilized by the conjugation of the electron-donor amino group in the coupling component with the carbonyl group in the phthalimide residue.

In saturated solutions in cyclohexane, the phenylazobenzamides and phenylazophthalimides have similar absorption maxima (436–454 nm), indicating a similar effect of the carbonyl groups, irrespective of their orientation with respect to the azo moiety. Using the PPP-MO method, and benzamide derivatives as reference systems (**1**–**3**), the absence of conjugation of the amide group in the *meta* position with the dialkylamino residue has been confirmed. On the other hand, in phenylazophthalimide dyes containing two carbonyl groups such a conjugation has been found to occur, but between both the carbonyl groups. Because of this, the cyclic imide substituent acts as an overall acceptor substituent. Calculations for the 3-phenylazophthalimide isomers were made taking into consideration the twisting of the molecule around the N(7)–C(8) bond, because of steric hindrance factors.

Using the spectra of reference azo dyes **4** containing substituents of known Hammett σ-constants to determine the relationship between these values and the λ_{max} in cyclohexane, Hammett σ-values 0·38–0·75 have been determined for the phthalimide system and the highest of these values is comparable with the σ-value of the nitro group (0·78).

Using the PPP-MO method and Pestemer's rule, it has been shown that it is possible to predict the half-bandwidth of the absorption band as a measure of the colour intensity, using the relationship between the half-bandwidth and the Stokes shift. For all the phenylazophthalimide dyes studied, the half-bandwidth was about three times greater than the value of Stokes shift. For the calculations on the phenylazophthalimide dyes, modified PPP-MO parameters for the carbonyl groups have been applied and a good correlation obtained between calculated values and experimental values determined in cyclohexane. It was also concluded that the nitrogen atom in the five-membered imide ring does not participate in the conjugation, probably due to the influence of the two adjacent carbonyl groups. The application of these modified parameters makes it possible to predict spectral properties of this group of dyes, a factor which can be of practical significance.

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