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Halochromic Effects of Azophthalimide Dyes and their Prediction by PPP Method

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ABSTRACT

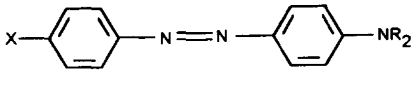
The spectra of azo dye derivatives of 3- and 4-aminophthalimide and their N-methyl derivatives in neutral and acid media have been recorded. The overall basicity constants (pK) have been determined by UV–VIS spectrophotometry. The values of these constants have been compared with those determined for simple derivatives of aminoazobenzene. The position of the absorption maxima for neutral and acidified dye forms have been calculated by the PPP method. It was concluded that the PPP method is useful to correctly predict the halochromic effect of the azophthalimide dyes even for non-planar molecules. Copyright © 1996 Elsevier Science Ltd

Keywords: Halochromic effect, azophthalimide dye, PPP method, azonium form, ammonium form, basicity constant.

INTRODUCTION

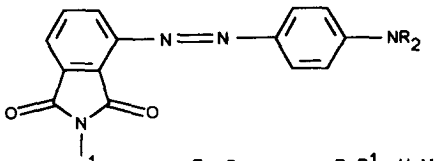
Phthalimide azo dyes **5**÷**12** constitute a relatively unknown group of disperse dyes with good functional characteristics,[1–5] the latter being due to the intermolecular association through hydrogen bonding. The dyes containing imide groups are characterized by a remarkable thermal stability and fastness to sublimation when dyed on polyester.[1,2,6,7] Their colour depends on the position of the azo group in the dye molecule, conformation and the type of *N*,*N*-dialkylamino group in the coupling component.

The susceptibility of dyes to acid media is of great importance from the point of view of their practical use in textile industries. The colour change during salt formation, known as halochromism, is undesirable in dyes



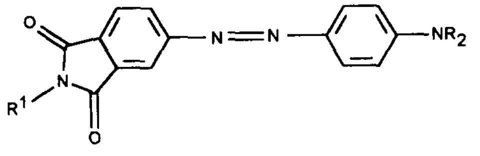
1 - 4

X = H, NO_2



5 - 8

R, R^1 = H, Me, Et



9 - 12

designed for textile dyeing, and is of use only in pH indicators. The extent of halochromism depends on the type of substituents present in the dye molecule.

From a practical point of view it is advantageous for the difference between the absorption maxima of protonated and unprotonated forms $(\Delta\lambda = \lambda^{hal}_{max} - \lambda^{abs}_{max})$ to be as low as possible. In some cases, the protonation of azo dyes can even result in complete decolourization.

Griffith and his co-workers[8] have used the PPP method to predict the halochromism of 4-aminoazobenzene derivatives. It seemed that the procedure could be used to examine unknown structures and to predict the suitability of phthalimide derivatives for practical use.

The colour of disperse dyes depends mainly on substituents with acceptor functionality. It is most advantageous in practical terms to provide the diazo component with more than one acceptor group, since such an addition makes it possible to obtain a strong bathochromic effect as well as a low dye susceptibility to acid media. Only very few acceptor substituents can occur in the 2,3- or 3,4-positions at the same time. Exceptionally, aminophthalimide derivatives, particularly the 1,2,3-isomers, have a considerable effect on the physical and chemical properties and electronic structure of their derived dye molecules.[2,6] The effect of substituents positioned in this way on dye properties has not been extensively examined.

Yagupol'skii[9,10] has reported the criteria for the evaluation of dye suitability for dyeing purposes. He has determined the limiting values of $\Delta\lambda$ which make it possible to classify dyes for textile dyeing or for use as indicators in acidimetry; he has also determined their dependence on Hammett σ substituent constants.

EXPERIMENTAL

The dyes under investigation were prepared and purified as described in the literature.[2,7,11,12]

The spectra of reference dyes **1**–**4** were recorded using their solutions in methanol at the following concentrations ($\times 10^{-5}$ mole/dm^3): **1**—6.04, **2**—5.96, **3**—7.11, **5**—3.90, **6**—4.08, **7**—3.90, **8**—4.08, **9**—4.64, **10**—3.94. The spectra of dyes **4**, **11** and **12**, due to their low solubility, were recorded using their saturated solutions. All the solutions were stored for 24 hr in the dark prior to spectral measurements. The λ_{max} measurements were performed with a SPECORD M-40 (Carl Zeiss-Jena).[13]

Solutions with various pH values were prepared as follows: to a 50 cm^3 measuring flask containing a dye, 0.00675 M H_2SO_4/MeOH was added in quantities from 1 to 10 cm^3.

The values of the basicity constant pK were calculated from the following equation:[13]

$$pK = pH + \lg \frac{D_A - D}{D - D_{HA}}$$

where D is optical density of the dye solution investigated, D_A the optical density of the solution containing only the neutral form of the dye, and D_{HA} the optical density of the solution containing a protonated form of the dye.

The values of overall basicity constants pK were calculated by the least-squares method.[13–16] The calculated values of λ_{max} for phthalimide dyes were taken from a previous paper.[6] In calculating data for the **5**–**8** (3-isomers), the twisting around N^1-$C_{phthalimide}$ bond by an angle of 30.0° was taken into account.[6] The halochromic effect was calculated by the PPP method using standard parameters;[17] modified values for carbonyl groups $C{=}0^6$ and the following values for protonated atom N^1: $A_Y = 12.50$ eV, VSIP $= 22.00$ eV, $\beta(C\text{–}N{=}N) = -2.75$ eV, $Z = 2$ were used.

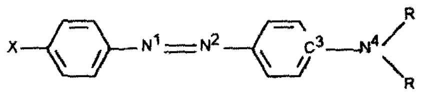
CALCULATION BY THE PPP METHOD

The calculations of neutral structures of the dyes under investigation are cited on the basis of calculations described previously.[6] The modification of parameters for protonated nitrogen atoms of the azo bond makes it possible to calculate the absorption spectra of dyes in acid medium (halochromic effect) with satisfactory accuracy (Table 1).

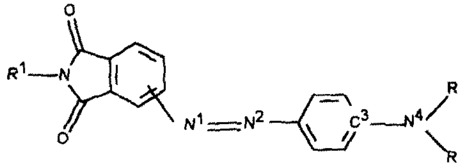
The use of the PPP method for quantum-chemical calculations and comparison of calculated and measured data requires the effect of solvent on spectra to be minimized. Since the dyes under study showed very poor solubilities in nonpolar solvent, they were dissolved in methanol. This solvent brings about dye molecule solvation both in neutral and protonated forms. This is shown by the absorption band shift by about 30 nm when compared

TABLE 1

Experimentally Determined Values of Basicity Constants and Experimental and Calculated Spectral Data for Model Dyes **1**÷**4** and Phthalimide Dyes **5**÷**12**



1 - 4



5 - 12

					Experimental				Calculated			
Dye		X	R1	R	pK^a	$\lambda_{max}^{abs\ b}$	λ_{max}^{hal}	$\Delta\lambda^c$	$\lambda_{max}^{abs\ d}$	$\Delta\lambda^c$	d_{C3-N4}	d_{N1-N2}
1	—	H		Me	3.26	411	522	111	398	129	−0.073	0.260
2	4-	NO$_2$		Me	2.72	488	511	23	445	64	−0.098	0.098
3	—	H		Et	3.83	420	520	100	409	116	−0.053	0.252
4	4-	NO$_2$		Et	3.03	496	511	15	459	47	−0.078	0.091
5	3-		H	Me	2.98	454	505	51	430	61	−0.112	0.044
6	30		Me	Me	2.88	456	502	46	426	65	−0.113	0.050
7	3-		H	Et	3.25	466	505	39	445	42	−0.094	0.035
8	3-		Me	Et	3.21	468	505	37	442	46	−0.093	0.040
9	4-		H	Me	2.82	466	511	45	441	61	−0.102	0.082
10	4-		Me	Me	2.69	473	514	41	439	64	−0.101	0.082
11	4-		H	Et	3.03	481	514	33	455	44	−0.082	0.072
12	4-		Me	Et	2.99	488	516	28	455	46	−0.082	0.077

d_{C3-N4}, d_{N1-N2}—changes in the bond magnitude in excited and ground state (positive value—bond elongation, negative value—bond shortening).

[a] Overall basicity constants with the protonation at azo and *N*,*N*-dialkylamine groups being taken into account. [b] Spectra recorded in methanol (**4**, **11** and **12**—saturated solutions). [c] $\Delta\lambda = \lambda_{max}^{hal} - \lambda_{max}^{abs}$. [d] VSIP (C=O) 18.10, (N–CH$_3$) 21.00, (N–H) 24.65; A$_y$ (C=0) 3.15, (N–CH$_3$) 10.00, (N–H) 10.15.[6,17]

with spectra in cyclohexane[6] (for non-protonated structures); such an effect should be taken into account in correcting initial parameters for calculation. A similar extent of λ_{max} shift connected with solvent replacement (solvatochromic effect) has been reported by other authors.[8]

RESULTS AND DISCUSSION

Until now it has been known that the performance properties of phthalimide dyes can be changed depending on the presence of substituents in the imide residue. The formation of intermolecular hydrogen bonds by these compounds is of decisive importance.[2–5] The colour of phthalimide dyes can be affected by amide-iminol tautomerism,[14,18,19] dye conformation,[14–16,20,21] as well as the type of substituent R at the imide nitrogen atom.

Simple aminoazobenzene derivatives (1–4) were used as reference compounds. The basicity constants of the dyes under study and initial parameters for calculating the extent of halochromism were determined. Moreover, it was necessary to take into account the steric hindrance in 3-aminophthalimide derivatives[6,22] due to which these dyes show a hypsochromic effect. Explanations of the consequence of steric hindrance in other azo dyes have been examined and described in the literature.[20,23–28]

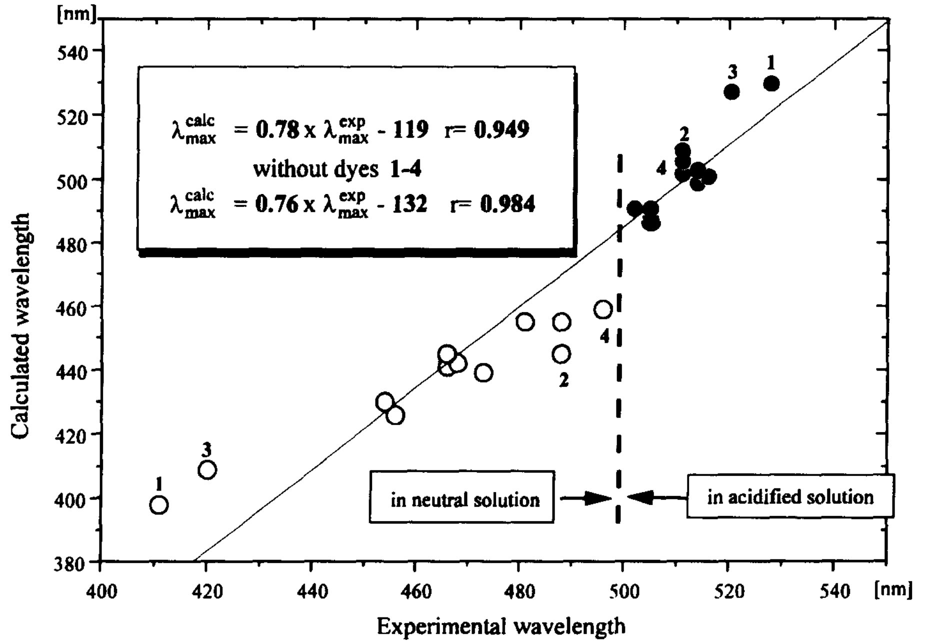
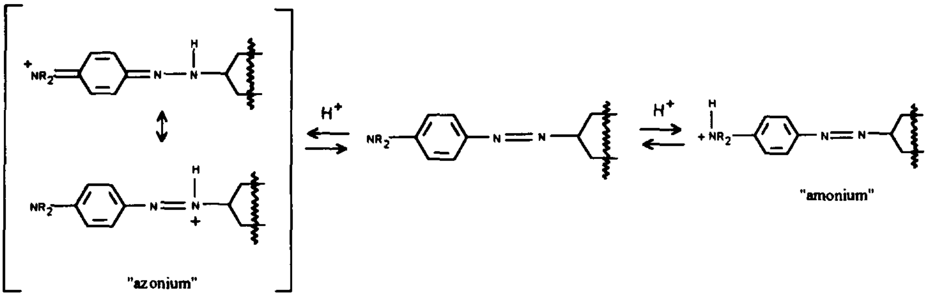


Fig. 1. Plot of calculated against experimental λ_{max} values for the dyes in neutral and protonated forms.

The present measurements included the determination of overall basicity constants resulting from the presence of electron donor groups in a molecule: both amine groups -NR_2 and azo groups -N=N-. The corresponding 'azonium' and 'ammonium' forms occur in an equilibrium whose position depends on the medium acidity, type of substituents and dye conformation. The observed deepening of colour in the acid medium results from the predominating 'azonium' form and the mesomerism of limiting structures.



The 'azonium' form shows an absorption within the range above 500 nm, while the 'ammonium' form absorbs within 300–350 nm.[28] The difference in λ_{max} between the 'azonium' and neutral forms is a measure of halochromic effect $\Delta\lambda$, which makes it possible to determine the dye suitability for practical purposes.

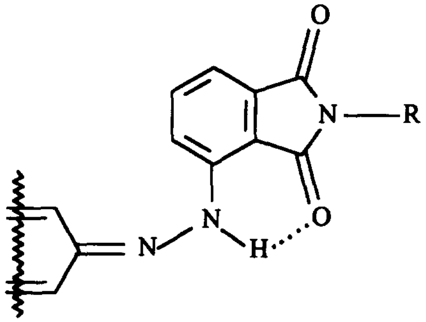
In acid medium most azo dyes show a positive halochromism whose extent depends on the strength of additional substituents present in the dye molecule.[8–10,13,23,25,26,28–31] The protonation results in considerable changes in or even complete disappearance of colour of the protonated dye.

Reference dyes **1** and **3** show very high halochromism values and when X=H they are 111 and 100 nm, respectively. The halochromic effect of dyes **5–12** is within the range 28–51 nm (Table 1).

The p*K* values determined allow us to establish quantitatively the effect of steric factors and substituents at the imide nitrogen atom on the spectral properties of dyes (Table 1).

The higher values of p*K* for the 3-isomers are in accord with an additional intramolecular stabilization of the 'azonium' form by hydrogen bonding.

Based on the measurements performed, the *N*,*N*-diethylamino derivatives showing the lowest halochromic effect ($\Delta\lambda$ = 28–39 nm) could be successfully used for practical purposes; less advantageous would be the use of *N*,*N*-dimethylamino derivatives with higher $\Delta\lambda$ values ranging from 41 to 51 nm. There is quite a good agreement between the experimental and calculated data (Table 1).



The strongest effect on the experimental values of p*K* and $\Delta\lambda$ is shown by *N*,*N*-dialkylamino residues. The bathochromic effect of the *N*,*N*-diethylamino residue (**7**, **8**, **11**, **12**) in relation to *N*,*N*-dimethylamino (**5**, **6**, **9**, **10**) is 12–15 nm. There is a good correlation between the $\Delta\lambda_{\max}^{calc}$ *and* $\Delta\lambda_{\max}^{\exp}$ values:

$$\lambda_{\max}^{calc} = \mathbf{0.78} \times \lambda_{\max}^{\exp} - \mathbf{119} \quad r = \mathbf{0.949}.$$

Even better agreement between the experimental and calculated values is observed when the analysis is confined only to the phthalimide dyes. The correlation coefficient of the function $\lambda_{\exp}^{calc} = f(\lambda_{\max}^{\exp})$ for dyes **5–12** is then $r = 0.984$. This supports the necessity of taking into account conformational effects caused by the non-planarity of the dye molecule when calculating the parameters for this group of dyes (Fig. 1).

The low susceptibility of *N*,*N*-diethylamino derivatives to acid media can be accounted for by the higher molecule polarization of the dye in the ground state, which is confirmed by lower changes in bond length **N^1–N^2** and **C^3–N^4** (Table 1) and corresponding changes in the excited state electron density calculated by the PPP method (Table 2). The shift of electron density towards the azo group is shown by higher p*K* values which suggest that the equilibrium between the 'azonium' and 'ammonium' forms should be shifted in favour of the former.

TABLE 2

Calculated Changes of π-Electron Densities in Excited State for Dyes **1**, **2**, **5**, **9**

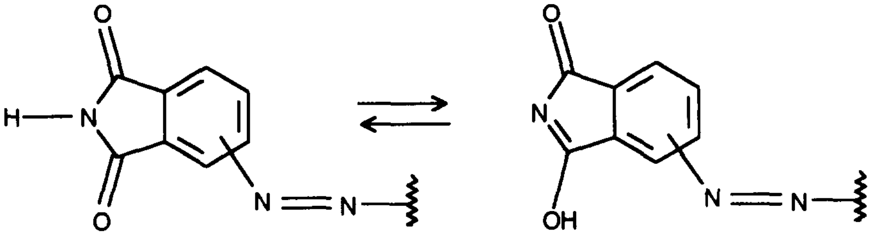
	N^1	N^2	C^3	N^4
1	+0.16	+0.27	+0.02	−0.30
2	−0.05	+0.07	−0.03	−0.35
5	+0.03	+0.01	−0.02	−0.33
9	−0.01	+0.14	−0.02	−0.33

−, decreasing; +, increasing electron density.

Similar changes take place during excitation of the molecule and result in increase of electron density at the nitrogen atoms of the azo bond, equalization of bond length of the conjugated system, averaging of the molecular electron density, manifested by a bathochromic effect.

The considerations took no account of the conformation analysis of dyes (*cis–trans* isomerism) since it is only possible in specific cases. The lifetime of the *cis*-isomer is very short and the isomer quantity is low in relation to the *trans*-isomer.[14,20,26,27,31–34]

It has been found in many examples that the imides can exist in an equilibrium of amide and iminol tautomeric forms. It is assumed that the equilibrium takes place in organic compounds containing the amide function.[14,18,19,35,36]



The slightly higher values of p*K* of the imide derivatives (N–H) in relation to N-methyl analogous (N-Me) suggest the existence of the imide derivatives as a equilibrium of the amide-iminol tautomeric forms. This conclusion is in accord with the wavelength changes (λ_{max}^{abs}) of the imide derivatives, which show a slight hypsochromic effect, from 2 to 7 nm, compared to the N-methyl derivatives. This effect is probably caused by the diminished acceptor character of the imide residue for the compounds with the -NH group due to formation of the iminol tautomer, which is not possible for dyes with the -NMe group.

Imide residues have an acceptor character (Table 1) due to the presence of carbonyl groups. The lack of co-planarity of the phenylimide residue in relation to the phenylazo residue in 3-aminophthalimide derivatives (**5–8**) should first decrease the effect of the N-R substituent on the molecule electron structure. The results obtained indicate that the type of N-imide substituent which affects the dye spectral properties should not be neglected in the considerations.

CONCLUSION

The spectral measurements of phthalimide azo dyes and the calculations of their electron structures by the PPP method made it possible to determine the effect of structural factors on the properties of those dyes.

It has been found that the *N*,*N*-dialkylamino substituent determines the molecule's susceptibility to the action of acid. From this point of view it is more advantageous to use the *N*,*N*-diethylamino substituent than *N*,*N*-dimethylamino. The nature of the imide ring has a weaker effect on halochromism. Some part is also played by the steric effects occurring in the 3-isomers.

The shift of absorption maxima of the protonated forms ($\Delta\lambda$) has been calculated by the PPP method, the results obtained being consistent with the experimental data. It has been found that due to the low $\Delta\lambda_{max}$ value of the protonated and neutral forms, the dyes under investigation can be used as dyes for textile dyeing purposes. This is additionally confirmed by their good performance properties.

Based on the changes observed in the values of basicity constants (pK) and wavelength determined, it can be suggested that the properties of azophthalimide dyes can be also influenced by amide-iminol tautomerism of the five-membered imide ring.

The present findings and literature data make it possible to predict the changes in properties of the examined dyes, associated with their structural variations. Thus, it is possible to make an optimal selection of dye structure with required performance properties. The comparison of the predicted and observed halochromism phenomena points to the fact that the PPP method can be successfully used to predict the changes in λ_{max} depending on the type of substituents in the ring, including the systems in which additional steric effects can occur.

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