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Structure–property Relationships in Azo Disperse Dyes, Derivatives of Naphthalimide

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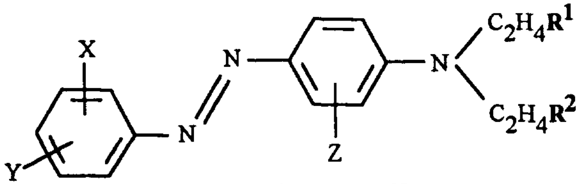
ABSTRACT

Spectrophotometric measurements of azo-naphthalimide dyes in which the coupling component is substituted by various N,N-*dialkyl substituents have been carried out. The absorption maxima of the dyes, their halochromic effect, and fluorescence spectra have been calculated by the PPP-MO method. A relationship was found between the* σ_x *of substituents and the input parameters for the calculations by the PPP-MO procedure.* © *1997 Elsevier Science Ltd. All rights reserved*

Keywords: naphthalimide dyes, PPP-MO method, halochromic effect, Stoke's shift.

INTRODUCTION

The performance properties of disperse dyes based on 4-aminoazobenzene **1**, are considerably influenced by the nature of the substituents R^1 and R^2.



$X,Y,Z = H, Cl, CH_3, OCH_3, NO_2$...

$R^1, R^2 = H, OH, OAc, CN$

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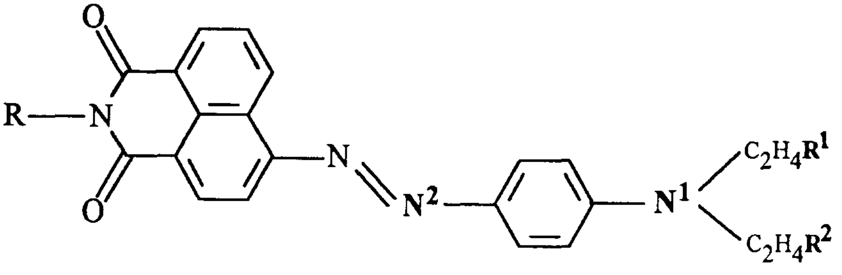
Because of their strong bathochromic influence, the use of dyes with *N*,*N*-diethylamino residues is especially advantageous,[1-4] but for other specific requirements, bring about a practice in dye synthesis where the terminal *N*,*N*-dialkyl groups can be substituted by, for example, cyano, acetoxyl or hydroxyl groups, as in dyes **2** and **3**.



R^1, R^2 = **a** (H,H); **b** (H,OH); **c** (H,OAc); **d** (OH,OH); **e** (H,CN); **f** (OAc,OAc); **g** (OH,CN); **h** (CN,OAc); **i** (CN,CN);
2 R = H;
3 R = CH_3

The effect of the R^1 and R^2 substituents on the dye performance properties is well recognized and is theoretically foreseeable, although only limited data concerning the effect of these substituents on dye spectral properties are available. Since such substituents are at the end of the aliphatic chain, their influence on colour would be expected to be minimal. Changes in spectral characteristics brought about by R^1 and R^2 can result only from inductive factors since these residues are isolated from the nitrogen atom (N^1) by up to three C–C bonds. The influence of the R^1 and R^2 substituents has previously been examined only for some simple 4-aminoazobenzene derivatives, and their effect on $\Delta\lambda$ was found to be relatable to their inductive σ_I constants.[4]

In this present study, an attempt is made to quantitatively determine the effect of the *N*,*N*-dialkylamino residue on the colour properties of some 4-aminonaphthalimide (**2**) and *N*-methyl-4-aminonaphthalimide dyes (**3**) by means of spectrophotometric measurements, in conjunction with PPP-MO calculations of the electronic structure of the molecules. In previous PPP-MO studies, the nature of the terminal substituent R has not been taken into account, in accordance with the inherent assumptions of the PPP-MO method. However, the observed large differences in the colour of the naphthalimide dyes investigated necessitated us to consider the effect of the R^1 and R^2 in the set of input parameters used for the calculations.

The studies were aimed also at an evaluation of the possibilities of applying the PPP-MO method for the determination of the colour properties of this group of dyes. The values of λ_{max}, theoretical positions of fluorescence bonds, half-widths of the absorption bonds, and halochromism factors were calculated, and the electronic structural changes of the dyes in the excited state were determined. Standard input data and modified values for the carbonyl groups of the cyclic imide systems were used in calculations. Relationships between calculated and experimental values were determined, on the basis that such results could be used in predicting some performance properties of naphthalimide azo dyes.

EXPERIMENTAL

The dyes were prepared using standard procedures: 4-aminonaphthalimide (**1**) and *N*-methyl-4-aminonaphthalimide (**2**) were diazotized and coupled with the appropriate *N*,*N*-dialkylanilines (**a**÷**i**) at pH 6.0–6.5. The dyes were purified by washing with 5% HCl at 90°C, then with water until neutral followed by boiling methanol, prior to recrystallisation from acetic acid.

Spectra of the dyes in methanol were recorded using saturated solutions. The solutions for measurements in acidified methanol were prepared in 50 cm^3 measuring flasks, adding 27.5 cm^3 of 96% H_2SO_4 solution to 10÷20 cm^3 of dye solution in methanol and making up to the mark with MeOH.

Spectra of dyes **2a, c, g, h; 1a, h** in chlorobenzene were taken using saturated solutions; the concentrations of the remaining dyes were: $1.7 \div 3.5 \times 10^{-4}$ M/dm^3. Spectra of dyes in *N*,*N*-dimethylformamide were taken using solutions with concentrations $3.0–5.1 \times 10^{-4}$ M/dm^3.

UV–vis spectra were measured at room temperature using a Specord UV–vis M40 spectrophotometer (Zeiss-Jena). Samples prior to measurements were stored in darkness for 24 h.

The calculations by the PPP-MO method were carried out using a standard set of parameters for neutral[5,6] and protonated[7] structures, and modified parameters for carbonyl groups in cyclic rings.[8,9] The fluorescence maxima were calculated using the procedure proposed by Lubai *et al.*[10]

RESULTS AND DISCUSSION

Spectra in methanol, *N*,*N*-dimethylformamide and chlorobenzene

The position of the dye λ_{max} is determined by the effect of solvent on the stabilization of the ground and excited states. Changes in the positions of the K-band ($\pi \rightarrow \pi^*$ shift) of the dyes under investigation in various solvents are brought about by the solvatochromic effect resulting from changes of the dielectric constant of the solvent (Table 1).[11,12]

One of the basic assumptions in PPP-MO calculations is the lack of solvent interaction and solvation. Therefore, in order to compare the observed and calculated spectral characteristics, measurements should be carried out in non-polar solvents. The naphthalimide dyes have only very limited solubility in cyclohexane and the concentration of even their saturated solutions made it impossible to perform measurements even in 10 cm cells. Therefore, the spectra of dyes **2, 3, a–i** were measured in their "neutral" solutions in MeOH, in acidified MeOH, and in DMF and chlorobenzene.

The dyes showed two absorption bands, characteristic of naphthalene derivatives.[13–16] Chromophore BAN, the so called IInd naphthalene band, absorbs within the range 360–364 nm and the possibility of its identification depends to a great extent on the position of the intense K-band, which can fall in a similar range. The position of the K-band is within the range 467–534 nm (in MeOH) and overlaps completely the R-band ($n \rightarrow \pi^*$).[15,17,18]

It was found that there was a distinct relationship between $\Delta\lambda_{max}$ and the nature of the substituents R^1 and R^2, and more precisely on the calculated value of the Hammett σ_x constant of the whole *N,N*-dialkylamino residue (Fig. 2). The best agreement between the experimental data and calculated values of σ_x was obtained using coefficient $\alpha = 0.10$, which takes into account the effect of substituents R^1 and R^2 on the basicity of the nitrogen atom (N^1) of the *N,N*-dialkylamino residue.

The value of σ_x was calculated from the following equation:

$$\sigma_x = \sigma_{Et} + \alpha \times \sum \sigma_I$$

where σ_{Et} is the Hammett constant of *N,N*-diethylamino substituent (0.902),[19] α is a correction coefficient taking into account the effect of R^1 and R^2 substituents on the basicity of the dialkyl nitrogen atom (0.10), σ_I is Taft's inductive constant for substituents: –OH (+0.16), –OAc (+0.33) and –CN (+0.53).[20]

In dyes where R^1 or R^2 is of an electron acceptor nature, the general character of the *N,N*-dialkylamino substituent, as measured by the Hammett σ_x value, remains electron donor. The substituent in the imide group (R = H, CH_3) only slightly affects the λ_{max} values and in order to simplify the theoretical considerations and calculations by the PPP-MO method, the effect of this substituent on the spectral characteristics of the dyes was neglected, on the basis that the imide nitrogen atom does not participate in the redistribution of electron density in the excited state of the dyes. Coefficients *a* and *b* and correlation coefficient *r* of the function $\lambda_{max}^{exp} = a \times \lambda_{max}^{calc} + b$ are shown in Table 2.

TABLE 1

Electronic Spectra for 4-Amino-*N*-methylnaphthalimides (**3a**÷**i**) and 4-Aminonaphthalimides (**2a**÷**i**)

Dye	*R*^{1},*R*^{2}	*MeOH*			*DMF*				*PhCl*	
		λ_{max}	$\Delta\lambda_{max}$	$\Delta\nu_{1/2}$	λ_{max}	lg ε_{max}	$\Delta\nu_{1/2}$	*f*	λ_{max}	lg ε_{max}
3i	CN,CN	455	113	—	492	4.21	5400	0.38	460	—
3h	CN,OAc	485	81	5200	506	4.36	5400	0.53	474	4.38
3g	OH,CN	500	68	5200	521	4.39	5100	0.54	485	—
3f	OAc,OAc	498	63	5600	512	4.22	5200	0.37	492	4.19
3e	H,CN	504	59	4900	514	4.18	5200	0.34	492	—
3d	OH,OH	514	47	5400	534	4.26	4900	0.39	498	—
3c	H,OAc	514	42	5300	525	4.37	4900	0.49	508	—
3b	H,OH	525	31	5100	537	4.36	4700	0.47	517	4.27
3a	H,H	534	26	4500	543	4.35	4700	0.45	527	4.38
2i	CN,CN	463	105	7500	492	4.36	5000	0.45	428	—
2h	CN,OAc	486	80	5500	498	4.39	5400	0.50	479	4.38
2g	OH,CN	490	78	5700	521	4.15	5400	0.33	472	—
2f	OAc,OAc	485	73	—	492	3.71	—	—	490	—
2e	H,CN	494	69	6000	514	4.09	5600	0.30	494	—
2d	OH,OH	496	62	—	525	3.70	—	—	472	—
2c	H,OAc	508	43	—	484	3.53	—	—	510	—
2b	H,OH	519	27	—	525	4.02	6200	0.28	502	—
2a	H,H	534	31	4500	541	4.42	4400	0.50	527	4.50

$\Delta\lambda_{max}$, difference λ_{max} between protonated and "neutral" of dye in [nm] (halochromic effect); $\Delta\nu_{1/2}$, band half-width in [cm^{-1}]; *f*, oscillator strength; ε(MeOH) = 32.6, ε(DMF) = 36.7), ε(PhCl) = 5.6.

TABLE 2

Relationship $\lambda_{max}^{exp} = a \times \lambda_{max}^{calc} + b$ for Dyes **2** and **3**

	2			**3**		
	a	*b*	*r*	*a*	*b*	*r*
MeOH	0.92	76.6	0.956	0.94	73.2	0.972
DMF	0.79	151.4	0.926	0.72	190.9	0.923
PhCl	1.08	−5.1	0.936	0.98	43.3	0.988
BAB (**1**)	0.61	167.1	0.968			

r, correlation coefficient.

The difference between the experimental and calculated λ_{max} values can be due to solvatochromic effects, i.e. dye–solvent interactions (solvation) and dye–dye interactions (association). This is particularly probable for the imide derivatives **2**, which can form intermolecular hydrogen bonds.[21–23]

The calculation procedure used was verified with simple 4-aminoazobenzene dyes (referred to as benzenazobenzene, BAB, in Table 2). They were used to perform comparative examinations with calculated data, using the parameterization as in the method described previously[5–7] (Table 3). It was found that the proposed procedure to predict the colour with respect to the type of substituent R^1 and R^2 was of a general nature and was suitable to be used both for the simple BAB dyes and for more complex dyes such as the azonaphthalimide derivatives.

The correlation coefficients of the function $\lambda_{max}^{calc} = f(\lambda_{max}^{exp})$ of the 4-aminoazobenzene benzenoazobenzene derivatives (**1**) and those of the naphthalimide dyes (in MeOH) are similar (Table 2). This makes it possible to precisely foresee the spectral properties of dyes with different substituents R^1 and R^2 and confirms the validity of the calculation procedure used. This factor is of importance, since alteration of the substituent at the end of the alkyl group considerably affects dye properties and the use of some substituents, particularly those of a strong electron acceptor nature, such as substituents **CN** and **AcO** brings about a considerable hypsochromic effect.

As with most azo dyes, the naphthalimide dyes under investigation undergo halochromism as a result of protonation of the azo bond in acidic solutions. The basic measure of dye resistance to the effect of acid media is the absolute value of the K-band shift (Δλ_{max}ˆ{hal}). Knowing Δλ_{max}ˆ{hal} of the protonated and neutral forms, one can determine the suitability of dyes for dyeing applications.[22–24,30] A low susceptibility of dyes to acids justifies their use for textile dyeing.

The experimental results show that the substituents R^1, R^2 affect the halochromism to an extent which depends on their donor or acceptor

TABLE 3
Calculated and Observed Values of λ_{max} for 4-Aminoazobenzene Derivatives (**1**)

R^1,*R*^{2}	*CN,CN*	*AcO,CN*	*OH,CN*	*AcO,AcO*	*CN,H*	*OH,OH*	*AcO,H*	*OH,H*	*H,H*
λ_{max}^{calc}	356	363	371	375	379	384	390	397	408
[a]	−0.106	−0.146	−0.194	−0.218	−0.238	−0.261	−0.282	−0.301	−0.323
λ_{max}^{exp}	382[3,4]	—	398[4]	—	400[4]	407[3]	—	—	415[3]

[a] Electron density changes at nitrogen atom N^1 in the excited state of the molecule.

character. Acceptor substituents bring about a hypsochromic effect since they decrease the molecule polarization, acting competitively in relation to the carbonyl groups in positions 1 and 8 of the naphthalimide ring. At the same time, dyes with substituents such as in **2i** (R^1, R^2 = CN) are most susceptible to acid due to the decreased electron availability at the nitrogen atom N^1 of the *N*,*N*-dialkylamino group and the increase in electron density at the nitrogen atom N^2 of the azo bond. The correlation coefficient of the relationship $\Delta\lambda_{max}^{hal} = f(\sigma_x)$ for the 4-aminonaphthalimide derivatives (**2**) was $r = 0.927$ and that for 4-amino-*N*-methylnaphthalimide (**3**) $r = 0.988$.

Of the readily available solvents with low dielectric constants ($\varepsilon = 5.6$),[11,12] chlorobenzene was used. This solvent slightly solvates the molecules of the compounds dissolved in it. Unfortunately, it was not always possible to obtain in this solvent solutions with concentrations high enough to perform a complete spectral analysis. For some dyes it was possible to obtain saturated solutions of unknown concentrations, and to evaluate only the solvatochromic effect. The results confirmed that in PhCl the spectral characteristics of the dyes were considerably affected by intermolecular aggregation and amido–iminal tautomerism of the imide ring, i.e. the same factors which, among others, determine the spectral properties of naphthalimide dyes in MeOH and DMF.

The values of the correlation coefficients of the function $\lambda_{max}^{calc} = f(\lambda_{max}^{exp})$ are of a similar order of magnitude as in MeOH and DMF, belonging to similar accuracy classes[25] (Table 2). The low values of the correlation coefficient of this function for derivatives **2a**÷**i** result from the intermolecular association of these dyes.

The overall results allow the evaluation of the solvatochromic effect, and show that the recording of spectra in MeOH instead of in PhCl results in only a slight bathochromic effect. Measurements on these naphthalimide dyes can thus be effected in MeOH and DMF without making significant errors. It is also clear that the substituents R^1, R^2 play only a minor role and have a weaker effect on the molecule polarization when compared with the azo bond. This is quantitatively illustrated by the value of coefficient α in the proposed equation for the calculation of the σ_x constant for the *N*,*N*-dialkylamino substituent.

Half-widths of the absorption bands in MeOH and DMF were also determined (Table 1). In addition to the effect on λ_{max}, substituents R^1, R^2 also cause a change in the half-width values. The value of $\Delta\lambda_{1/2}$ (or $\Delta\nu_{1/2}$) is a convenient criterion for the evaluation of the hue brightness of dyes. Dyes with low $\Delta\lambda_{1/2}$ show bright hues (hyperchromic effect) while those with high values of $\Delta\lambda_{1/2}$ show dull hues (hypochromic effect). It has been found that the half-widths of the absorption bands of the investigated dyes are of similar order of magnitude as for the simpler derivatives **1** and are dependent on the type of solvent used.[26] These factors have been previously described for phthalimide derivatives.[8]

A significant observation is that the highest $\Delta\nu_{1/2}$ values are shown by the derivatives in which R^1 and R^2 are acceptor substituents (**–CN** and **–OAc**). This testifies to the presence of additional absorption bands with shifted maxima in the spectra and is revealed by a slight hue dullness of the dyes. The brightest hue is shown by the dyes with the *N*,*N*-diethylamino substituent (**1, 2a**, R^1, R^2 = **H**), for which $\Delta\nu^{1/2} = 4500 - -4700\ cm^{-1}$ both in MeOH and DMF.

Dull hues were mainly observed in the case of acceptor substituents in the aliphatic chain, which implies the necessity of taking into account the interactions between substituents in the aliphatic chain. The disturbance of the spatial structure must result in reduction of the conjugation effect and a hypochromic effect in relation to the dyes in which such interactions cannot take place. Moreover, the absorption curves of such dyes are asymmetric, which indicates that the values of the oscillator strength f, as calculated from spectral characteristics, are not free from error and that it is difficult then to compare them with the values calculated by the PPP-MO method, which neglects such interactions.

The naphthalimide dyes can, however, also exist in the form of a tautomeric amide–iminol equilibrium of the imide ring. This effect reduces the acceptor character of substituents such as carbonyl groups. It is difficult to observe this phenomenon, since this factor overlaps others, e.g. those connected with the specific reactivity of positions 1 and 2 in the naphthalene ring or the inductive effect of substituents at the *N*-imide nitrogen atom.

Calculation of spectra by the PPP-MO method

Calculation by the PPP-MO method of the electronic state of dyes containing naphthalimide residues has not been previously reported. The method is usually used for the calculation of molecules with conjugated π-bonds. No parameterization exists for the input data for "isolated" systems such as substituents R^1 and R^2.

In order to optimise the use of the PPP-MO method for the naphthalimide dyes **2** and **3**, calculation parameters were modified on the basis of changes in the σ_x values (Table 4). Thus, it was possible to quantitatively determine the donor character of N^1 and to take into account, at the same time, the change in character of the substituents R^1, R^2 isolated from the conjugated system. To that end it was necessary to determine the relationship between the calculation parameters VSIP and A_y and the variable values of σ_x.

TABLE 4

Electronic Spectra Data of Dyes **3a**÷**i** Calculated by the PPP-MO Method

Dye	R^1,R^2	σ_x	$VSIP/A_y$	*Absorption*			*Halochromism*		*Fluorescence*	
				λ_{max}^{abs}	N^1	M	$\Delta\lambda_{max}^{hal\ a}$	$\Delta\lambda_{max}^{hal\ **}$	$\Delta\lambda_{max}^{fsc}$	S
3i	CN,CN	0.79	20.6/11.8	429	−0.074	9.17	158	142	54	2600
3h	AcO,CN	0.81	20.1/11.0	436	−0.111	9.70	156	137	53	2500
3g	OH,CN	0.83	19.6/10.2	445	−0.162	10.38	151	129	51	2300
3f	AcO,AcO	0.84	19.4/9.8	451	−0.189	10.78	145	122	47	2100
3e	CN,H	0.85	19.1/9.5	456	−0.212	11.11	141	116	43	1900
3d	OH,OH	0.86	18.9/9.1	464	−0.239	11.59	132	106	41	1750
3c	AcO,H	0.87	18.7/8.7	471	−0.263	12.10	122	97	39	1600
3b	OH,H	0.88	18.4/8.3	479	−0.284	12.69	112	85	35	1400
3a	H,H	0.90	18.0/7.5	494	−0.311	13.97	88	62	30	1200

λ_{max}^{abs}, calculated absorption maximum; calculated $\Delta\lambda_{max}^{hal}$ and $\Delta\lambda_{max}^{fsc}$ $(\Delta\lambda_{max}^{hal(fsc)} = \lambda_{max}^{hal(fsc)} - \lambda_{max}^{abs})$ in [nm]; σ_x, calculated Hammett σ constant; VSIP, valence state ionization potential; A_y, electron affinity; N^1, electron density changes in the excited state; M, calculated dipole moment in [D]; * calculated using standard VSIP/A_y 22.00/12.50;[7] ** and modified set of parameters VSIP/A_y 21.50/10.50; S, calculated Stoke's shift in [cm^{-1}].

TABLE 5

Calculated and Observed λ_{max} Values for Dyes **3a÷i**

	λ_{max}^{abs}		λ_{max}^{hal}			$\Delta\lambda$*
				VSIP 22.00 A_y *12.50*	*VSIP 21.50* A_y 10.50	
	Exp.	***Calc.***	*Exp.*	*Calc.*	***Calc.***	
3a	534	**494**	545	582	**556**	62
3b	523	**479**	554	591	**564**	85
3c	514	**471**	553	593	**568**	97
3d	514	**464**	561	596	**570**	106
3e	504	**456**	563	597	**572**	116
3f	498	**451**	561	596	**573**	122
3g	498	**445**	566	596	**574**	129
3h	485	**436**	566	592	**573**	137
3i	467	**429**	580	587	**571**	142

* Difference in absorption ($\Delta\lambda = \lambda_{max}^{hal} - \lambda_{max}^{abs}$) calculated with the use of modified parameters (appropriate columns are marked with bold-faced print); VSIP, valence state ionization potential; A_y, electron affinity.

For these calculations we used the standard input parameters,[5,6,8] previously utilized for phthalimide derivatives and our own set of modified data for carbonyl groups[9] verified with the phthalimide derivatives.

The basis for evaluating the correctness of the assumptions for the modification of calculation parameters was spectral measurements of the dyes in various solvents. They also allowed the evaluation of the solvatochromic effect. A significant problem in the comparison of experimental and calculated λ_{max} is that it is impossible to carry out spectral measurements of the naphthalimide derivatives **2a÷i** in non-polar solvents. The best solvent is DMF, which, however, gives the strongest solvatochromic effect. Although the dyes are not very soluble in MeOH and PhCl, it is possible to determine the basic spectral parameters, which are helpful for comparison with data calculated by the PPP-MO method (Table 5).

The analysis was confined to derivatives **3a÷i** to avoid problems connected with dye solubility and the effect of intermolecular association on their spectral characteristics.

It was found that the best agreement between calculated and experimentally found λ_{max} values for the *N*-methyl derivatives **3** was obtained for linear functions [VSIP, A_Y] $= f(\sigma_X)$:

$$[\mathrm{VSIP}] = 28.7 - -23.5 \times \sigma_X$$

$$[A_y] = 52.8 - -38.7 \times \sigma_X$$

The calculated values of λ^{abs}_{max} of the dyes are in a quite good agreement with those found in MeOH after taking into account the solvation effect of the solvent on the dye molecules, which results in a bathochromic shift in the region of 10–30 nm.[18] The directions of changes are also consistent with the inductive properties of the terminal substituents on the aliphatic chains of the *N*,*N*-dialkylamino residues. Strong acceptor substituents such as –CN bring about the hypsochromic effect due to the reduced electron density on the nitrogen atom N^1.

Our calculation assumptions do not take into account the spatial configuration and mutual electrostatic interaction of the substituents. The presence of substituents with a strong inductive acceptor character, e.g. **–CN**, results in such a considerable decrease of the electron donor character of the *N*,*N*-dialkylamino group that the observed absorptions (λ^{exp}_{max}) of dyes **3** are similar to those of dyes without donor substituents.[15]

The calculations of electronic structures were carried out only for the N-methylimide derivatives **3a÷i** (R = CH_3). It was found that neglecting the *N*-methyl substituent did not result in significant changes in the basic data (e.g. the calculated value λ^{calc}_{max} is different by 1–2 nm, while $\Delta\lambda^{calc}_{max}$ differs by 1–3 nm for extreme cases in relation to analogous derivatives **2a÷i**). Thus, it can be concluded that the general conclusions will be reasonable both for *N*-alkyl and unsubstituted imides.

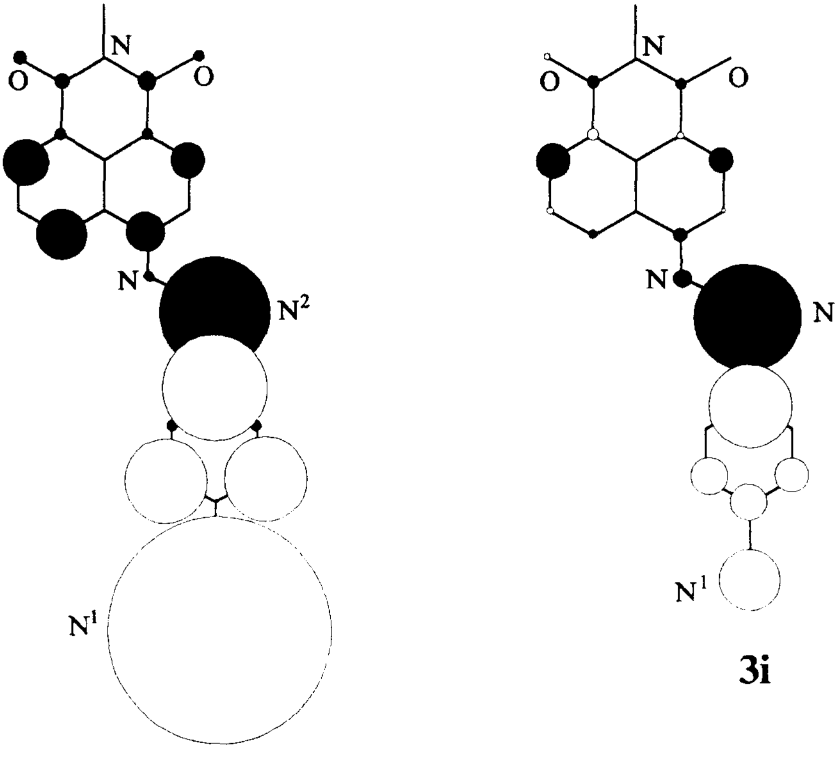
The best correlation between the calculated values of $\Delta\lambda^{abs}_{max}$ and σ_x was obtained for the *N*-methyl derivatives **3** (R = CH_3). The imide derivatives **2** (R = H) showed deviations from a linear relationship due to the influence of additional intermolecular effects on their properties. These phenomena have not been taken into account in hitherto performed calculations.[9,27]

The protonated structures of the examined naphthalimide dyes, reflecting their halochromism, were also calculated, using the basic set of data cited in the literature;[5-7] VSIP 22.00, A_y 12.50, β ($- - \mathbf{C} - -\mathbf{N} = \mathbf{N}$) 2.75 eV, $Z = 2$ (Fig. 2, [hal*]) and data derived from our own studies.[8,9,28]

It was seen that the correlation of the function $\Delta\lambda^{hal}_{max} = f(\sigma_x)$ was relatively unsatisfactory, and that the calculated values of λ^{hal}_{max} differed considerably from those found experimentally. In the case of dye halochromism, the solvent effects on the absorption maxima are only minor and the set of parameters was therefore optimized so as to obtain the best possible agreement between the calculated and observed values of λ^{hal}_{max} (VSIP 21.50, A_y 10.50, $Z = 2$). With this correction, the correlation of that function was considerably improved: $r = 0.988$ (Fig. 2, [hal**]).

The calculated values are consistent with those found experimentally for the substituents whose $\sigma_x \geq 0.85$, i.e. when R^1, R^2 = **OH**, **CN**. The change in electron density on shifting to the excited state is at the N^1 atom -0.189. Strong acceptor substituents bring about derivation from the linear character of the function $\Delta\lambda_{\max}^{\mathrm{hal}} = f(\sigma_{\mathrm{x}})$ and the calculated values are lower than the observed ones. This could be due to the mutual electrostatic and steric interactions of the substituents and a consequent change in the spatial configuration of the entire *N*,*N*-dialkylamino group. These substituents clearly affect the electron density redistribution and decrease the dipole moment of the molecule. The changes taking place in the dye molecule as a result of light absorption, depending on the nature of the substituents R^1 and R^2, are illustrated in Fig. 1, in which for clarity only derivatives **3a** and **3i** are shown. The relationship $\Delta\lambda_{\max} = f(\sigma_{\mathrm{x}})$ is much better illustrated by the curve with correlation coefficient $r = 0.999$.

The increase in electron density takes place in the excited state, particularly on the N^2 atom, and this is not solely due to the decreased electron density on N^1. The changes encompass the whole molecule — to a greater extent for



3a

3i

Fig. 1. Illustration of changes in the electron density in the ground and excited states of dyes **3a** (R^1, R^2 = H) and **3i** (R^1, R^2 = CN). Black circles show increase in electron density and their size is proportional to the extent of the changes.

dye **3a** and to a lesser extent for dye **3i**. The naphthalimideazo fragment is an acceptor of electrons and constitutes a "negative" fragment of the dipole, while the *N*,N^1-dialkylphenyl residue is a "positive" fragment. In dye **3i**, in which the substituents R^1 and R^2 (CN) have a strong acceptor character, the changes in electron density on N^1 are much smaller; they are also smaller in the phenyl ring conjugated with the dialkylamino group. As a result, the dye molecule dipole moment is also lower. The decreased polarization of the molecule in the excited state brings about a considerable hypsochromic effect when compared with that of dye **3a**.

Calculation of theoretical fluorescence spectra and hue brightness

The principles for the determination of dye hue brightness from the analysis of Stoke's shift were initially reported by Pestemer *et al.* in 1964,[29] who carried out measurements of 32 dyes of various types, determined the positions of their fluorescence bands and postulated the relationship between the Stoke's shift *S* and the half-width of the absorption bands. Basic theoretical concepts for the utilization of the PPP-MO method for the calculation of fluorescence band positions have been reported.[31-33] and have been practically used by Lubai *et al.*[10]

The calculations performed for the *N*-methylimide derivatives **3** show that this relationship can assume a similar form to that proposed by Pestemer, and is consistent with the equation:

$$\Delta\nu_{1/2} = 2.72 \times S[\times 10^{-3}\text{cm}^{-1}]$$

where the relative error is $+32.7 \div -23.5\%$ (Table 6). Its value is comparable with that determined by Pestemer and confirms the validity of the assumptions used in the method for theoretical forecasting of the width of absorption bands. Pestemer's rule was analysed on the basis of the collected experimental data (Table 1 and Table 4).

The analysis of values *a* (Table 6) shows a good agreement between the value $a = 2.50$,[29] given by Pestemer *et al.*, and the values calculated by the PPP-MO method. The accuracy of the results of the calculation is even

TABLE 6

Coefficients of Function $\Delta\nu_{1/2} = a \times S(-b\% \div +c\%)$

No.	*Dyes*	*a*	*b*	*c*
1	**2a÷i**	2.87	27.5	26.8
2	**3a÷i**	2.72	23.5	32.7
3	**2,3a÷i**	2.80	25.7	30.0
4	Pestemer rule[29]	2.50	23.2	46.8

higher than that of the experimental data obtained by Pestemer. Attempts have also been made to describe the relationship $\Delta\nu^{1/2} = f(S)$ in the form of linear functions,[10] but to confirm this theory, much more experimental material is required, together with data for a considerably higher number of derivatives. It seems that the relationship given by Pestemer is of a general character, and can be used for the examination of dyes in solution as well as on dyed fibres. The observed deviations from the average value, equal to 2.50, result from the specific structure of the dyes under investigation.

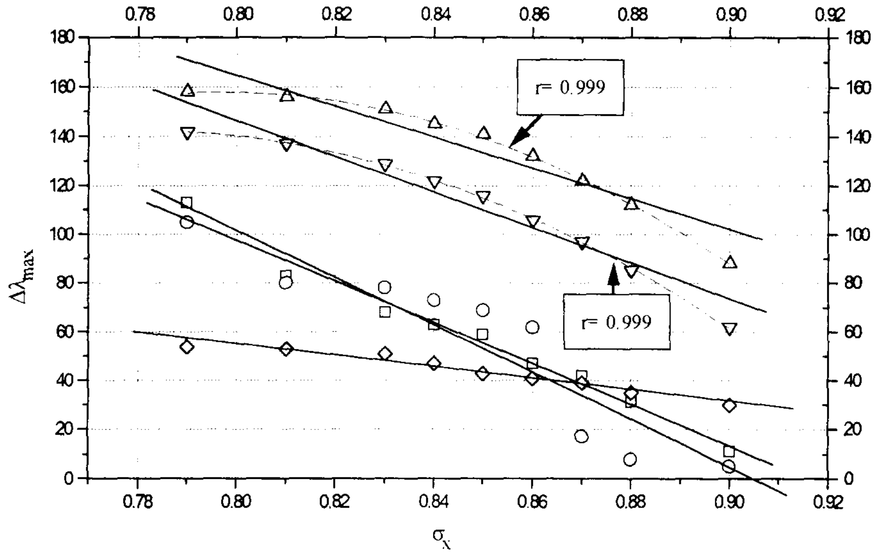
CONCLUSION

Spectral measurements and calculations of the electronic structures of 4-(*N*,*N*-dialkylaminophenyloazo)-*N*-methylnaphthalimide derivatives (**3**) and 4-(*N*,*N*-dialkylamino-phenylazo-naphthalimide derivatives (**2**) confirm the suitability of the PPP-MO method for predicting dye properties, even for systems where functional groups are not present in the chain of conjugated bonds. It has been found that their effect on the structure and spectral properties are well reflected by a simple linear relationship with the Hammett σ constant of the *N*,*N*-diethylamino substituent and the Taft inductive constants (σ_I) of substituents R^1, R^2. Both halochromism and the predicted position of the fluorescence bands can also be foreseen with satisfactory accuracy.

Calculations of the electronic structures of the dye molecules, carried out by the PPP-MO method, well reflect the changes in dye properties observed experimentally. Once the input parameters for calculation were modified, very high correlation coefficients with appropriate linear functions were obtained (Fig. 2). It should be noted that the curvature of the plots in Fig. 2 is probably due to the plot employing wavelengths, and not energies, against σ (which is a linear free energy parameter). It is possible to improve the correlation by introducing other input parameters to obtain a better agreement between the theoretical and experimental data. Whilst such attempts have been carried out,[35] but only for simple aromatic systems, they are much more difficult for dyes, since it is not fully possible to verify the correctness of the assumptions made.

The utilized set of parameters is of a general nature and suits well the calculation for derivatives with both 5-unit and 6-unit heterocyclic rings.

It is concluded that the parameterization used is adequate enough to predict some dye properties with good accuracy. All the modifications made in accordance with the rule of least interference with the program calculation parameters concern specific molecular structures. It would seem that the parameter changes made are sufficient to obtain a satisfactory agreement



□ **3a÷i** $\Delta\lambda^{abs}_{max} = 773 - 845\sigma_X$, r = 0.979; ○ **2a÷i** $\Delta\lambda^{abs}_{max} = 878 - 970\sigma_X$, r = 0.929,
△[hal*] $\Delta\lambda^{hal}_{max} = 665 - 627\sigma_X$, r = 0.938, ▽[hal**] $\Delta\lambda^{hal}_{max} = 520 - 743\sigma_X$, r = 0.988,
◇ [fsc] $\Delta\lambda^{fsc}_{max} = 242 - 234\sigma_X$, r = 0.975

Fig. 2. Experimentally found relationship $\Delta\lambda_{max} = f(\sigma_x)$ for dyes **3a÷i** (□) and **2a÷i** (○) and calculated relationships $\Delta\lambda_{max} = f(\sigma_x)$ for dyes **3a÷i** in the protonated form based on standard (hal*) (△) and corrected (hal**) (▽) data. (fsc) (◇) – Stoke's shift.

between theoretical and experimental data, and also to enable satisfactory predictions to be made of some properties of the dyes, such as the dye hue brightness from the Stoke's shift. Although the PPP-MO method is based on some simplified assumptions and takes into account only π-electrons, it can be practically utilized for dyes with cyclic imide rings.[31-34]

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