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Effect of the sulphonic group position on the properties of monoazo dyes

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Abstract

The colour properties of monoazo dyes, analogues of C.I. Direct Red 23 (CI 29160), containing a sulphonic acid group in the diazo component have been examined. Optimisation of the molecule geometric structure was carried out by the AM1 method, while the absorption maximum positions were calculated by the PPP-MO method. The calculated and found values are in good agreement. It has been found that the position of the sulphonic acid group significantly affects the molecule spatial structure and thereby the coupling effect. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: PPP method; AMl method; 6-Amino-1-naphthol; Sulphonic acid group; Spatial structure

1. Introduction

Our previous paper [1] described the properties of several disazo urea dyes, isomers of C.I. Direct Red 23 (CI 29160), containing sulphonic groups in various positions. It was found that, contrary to commonly accepted views, the position of the sulphonic groups in the dye molecule significantly affects the colour and other properties of the dyes. It was assumed that appropriate location of the sulphonic group could bring about a change in the spatial structure of the dye, resulting in considerable disturbances in the delocalisation of π electrons which are responsible for the dye colour.

In order to verify this, several model monoazo dyes with sulphonic groups in different positions **1o**, **1m**, **1p**, **St**, analogues of CI 29160, were synthesised and their spectra in aqueous solutions with various pH values were measured. Using quantum-chemical methods, the spatial structure of these dyes was optimised. Absorption maxima were calculated by the PPP-MO method, taking into account possible changes in the dye spatial structure.

2. Experimental

The dyes were synthesised by the method described earlier [1] and they were purified by repeated washing with hot buffer solutions at pH = 9.2.

2.1. Electronic spectra

Electronic spectra were run first in buffer solutions at pH = 6.82–13.36 and then within the pH range 9.00–10.24 (**1o–p**) or 12.22–13.36 (**St**), at concentrations 1.3–2.0 × 10^{-4} m/dm^3. Spectral

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analysis was carried out using a Specord M40 spectrophotometer (Zeiss Jena). The values of λ_{max} were determined by the analysis of second order spectra of the spectral curve.

2.2. Determination of pK_a

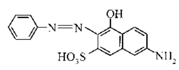
After determination of analytical wavelength, the precise pK_a measurement was carried out as described in the literature [2].

2.3. Calculation of geometry and absorption wavelength of dyes

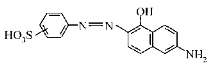
The optimisation of geometric structure and total molecule energy were calculated using HyperChem v.4.0 (of Hypercube, Inc.). The molecular structures were optimised at the AM1 level [3]. For the colour prediction, the standard PPP-MO calculation procedure was run [4,5], using a standard set of input data [4–8].

3. Results and discussion

Four model dyes, derivatives of 2-phenylazo-1-naphthol, with sulphonic groups in *ortho*-(**1o**), *meta*-(**1m**) or *para*-(**1p**) position in relation to azo bond or in the naphthalene skeleton were synthesised and used to examine the effect of sulphonic groups on their colour.



St



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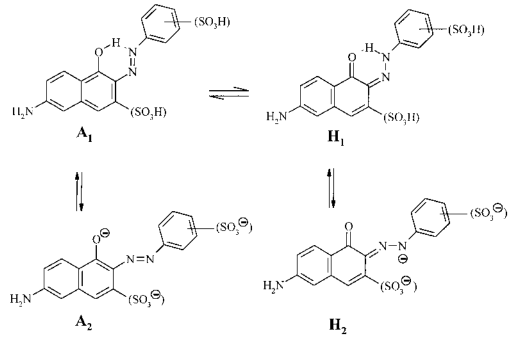
1o	*orto-*
1m	*meta-*
1p	*para-*

The dyes may occur in both the azo (**A_1**) and hydrazone (**H_1**) forms, being in equilibrium, and which can be respectively ionised (**A_2** and **H_2**):



Previous examinations of *o*-hydroxyazo compounds did not take into account the effect of the sulphonic groups in the dye molecule. Kuder [9] found that stabilisation of the hydrazone form was twice as high than that of the azo form, owing to the ability of the *ortho*-hydroxyazo systems to form intermolecular hydrogen bonds. As was calculated earlier, e.g. the hydrazone form of 2-phenylazo-1-naphthol absorbs at 490 nm (50% EtOH/water), with the hydrazo/azo isomer ratio being 3:1 under these conditions [10,11]. It was also found that this form is strongly stabilised by polar solvents such as water [12,13].

Study of the changes in the spectral characteristics in neutral and alkaline medium make it possible to determine the basicity constants of the imine groups of the hydrazone form and the azo/hydrazone equilibrium in the dyes [11]. They will influence the properties of the dyes, especially their sensitivity to alkaline medium.

Studies on other hydroxyazo compounds have shown that the colour of a compound strongly depends on the polarisation of the hydroxyazo system [14,15]. In presence of an amine group affects the colour to a lesser extent, and this depends on the change in its donor character as a result of acylation. As was previously shown, however, this effect is negligible [1].

In order to determine the position of bands ascribed to the azo and hydrazone forms in derivatives of phenylazo-1-naphthol containing a sulphonic group in different positions, spectrophotometric measurements were carried out, including analysis of second order spectra of monoazo dye (**St**, **1o**, **1m**, **1p**) in aq. solution at pH = 6.82 (Figs. 1 and 2) and in aq. solution at pH = 13.36; the results are given in Table 1.

3.1. Dye spectra at pH = 6.82

The analysis of second order spectra was used, since, as has been previously confirmed [16], it allows precise determination of the positions of absorption maxima, and even reveals those bands

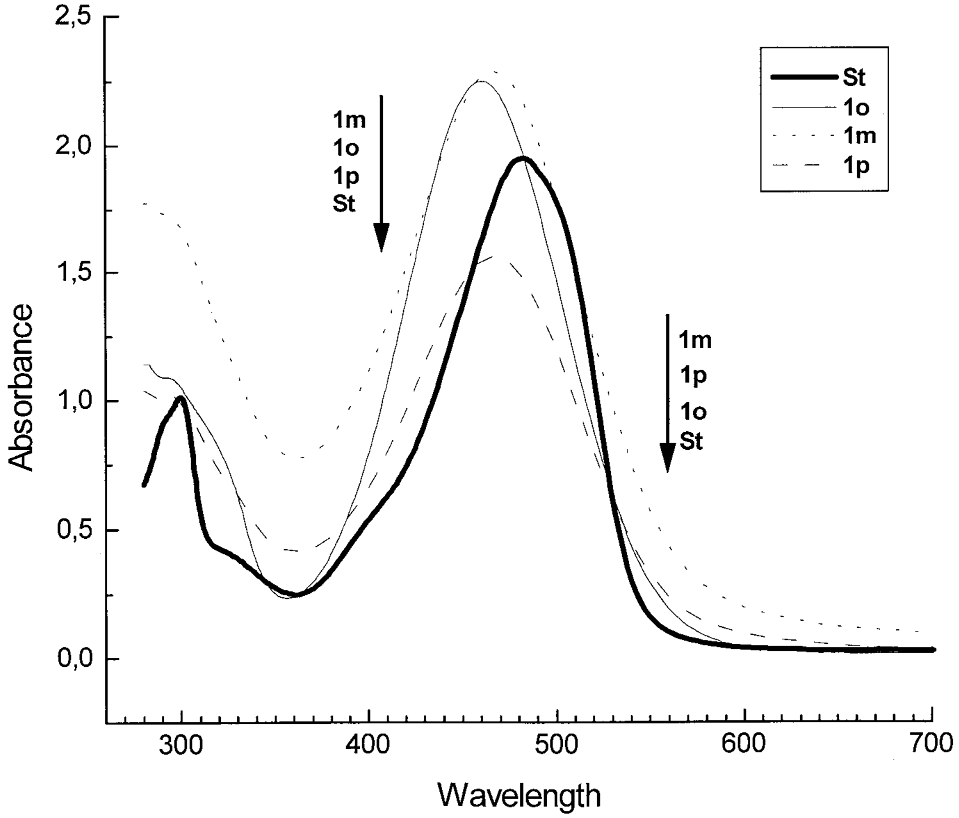


Fig. 1. Spectral characteristics of standard dye **St** and dyes **1o**, **1m** and **1p** in solutions at pH = 6.82.

Table 1
Experimentally determined positions of absorption maxima of dyes **St**, **1o**, **1m** and **1p**

	Form/dye	St	1o	1m	1p
pH = 6.82	H_1	478	465	470	480
pH = 13.36	H_2	506	518	522	537
	A_2	450	–	–	–

with low intensities which are difficult to identify due to their being masked with the more intense adjacent band [16]. Analysis of differential spectra (Fig. 2) indicates the presence, in the spectrum of standard dye **St**, of vibration bands of the hydrazone structure at 478 and 506 nm, which shows that they result from two independent electronic excitations, in accordance with the observations of Mustroph [17]) and Stojanov [18]) for similar compounds. These bands are believed to result from dye aggregation, while the band with a lower energy (higher wavelength) belongs to the aggregated form of the dye [19]) . To show that, in the considered case, the existence of two bands is not the result of aggregation, the decay rate of bands at 478 and 506 nm versus pH was analysed. It was shown that the rate is constant; thus, the observed presence of two absorption bands is not due to aggregation, but rather indicates the vibronic origin of these bands resulting from interactions between independent electronic excitations $n_s\pi^*$ and π,π^* [18,20–22]. In dyes **1o**, **1m**, **1p** at pH = 6.82, only single bands of the dye hydrazone form can be identified.

3.2. Dye spectra at pH = 13.36

The position of bands at pH = 13.36 corresponds to the ionic form of dye A_2 or H_2.

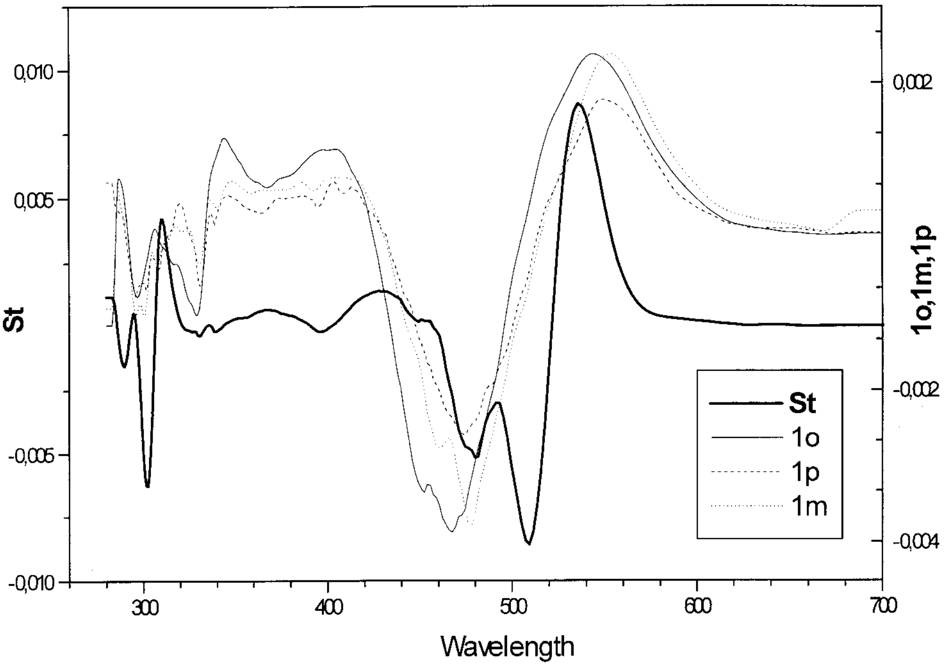


Fig. 2. Differential spectra (second order spectra) of dye **St** and **1o**, **1m**, **1p** (pH = 6.82).

All the examined dyes at pH = 13.36 absorb within the range 506–537 nm. The hydrazone form of the *ortho*-hydroxyazo dye also absorbs within this range. Detailed analysis of second order spectra indicates, however, the presence of an additional band at 450 nm in the standard dye **St** (Fig. 3a, Table 1).

The curves for dyes **1o** and **1p** are the same as that for dye **1m** (Fig. 4). Analysis of the spectral characteristics at various pH values, confirmed by PPP-MO calculations, allow us to conclude that the band at 520–540 nm (**1m**, **1p**) is derived from the ionic hydrazone form $\mathbf{H_2}$ (506 nm–**St** and 518 nm–**1o**).

Double bands can be clearly identified (Figs. 3 and 4) in the standard dye **St** at pH = 6.82, while their position cannot be unmistakably determined in the remaining dyes. At pH = 13.36 a band at 450 nm appears in dye **St**, in addition to the band of the hydrazone form $\mathbf{H_2}$ at 478 nm (Fig. 3). The origin of the 450 nm band can be ascribed to the ionised azo form $\mathbf{A_2}$. The band of the hydrazone form decreases and the spectral characteristics show no isosbestic point. This observation also appears in dyes **1o–p**, and the absorption maxima are shifted in a bathochromic manner. This indicates the existence of other types of equilibrium in solution.

The spectral characteristics of dyes **1o–p** are considerably different from those of the derivatives of 2-phenylazo-1-naphthol [15,23]. The fact that the variation in pH of solution brings about considerable changes in the spectral characteristics and the appearance of a long-wavelength absorption of form $\mathbf{H_2}$ indicates that, in these dyes, the *ortho*-hydroxyazo system is stabilised to a low extent by intermolecular hydrogen bonding, a factor which was previously found by Skulski [23] who examined simple models. These dyes are ionised up to 20% (Fig. 4) at pH = 8.3–9.0. A similar degree of ionisation is reached by dye **St** only at pH≈11.2 in the form of $\mathbf{A_2}$. The changes in the spectral characteristics of dyes **1o–p** at various pH values are similar to those observed for 4-phenylazonahthol-1 derivatives in which no additional molecule stabilisation with hydrogen bonds was found [20,23–25].

The quantitative changes in hydrazone forms versus pH of solution can be calculated according to the following relationship:

$$[\%\ \text{of jonic form}) = \frac{A_x - A_{H_1}}{A_{H_2} - A_{H_1}} \times 100$$

where: A_x, A_{H_1}, A_{H_2} — absorbance at the analytical wavelength and absorbances of dye at pH = 6.82 and 13.36, respectively.

The analytical wavelength for each dye was determined as the wavelength for which the difference in absorbance between ionic and neutral forms was the highest. Their values were: 478 nm for dye **St**, 448 nm for **1o**, 451 for **1m** and 457 nm for **1p** [2].

In calculation of the percentage of ionic forms, it was assumed that the dye appears in the unionised form in neutral medium and in a completely ionised form in alkaline medium. This makes it possible to determine the acidity of the imine

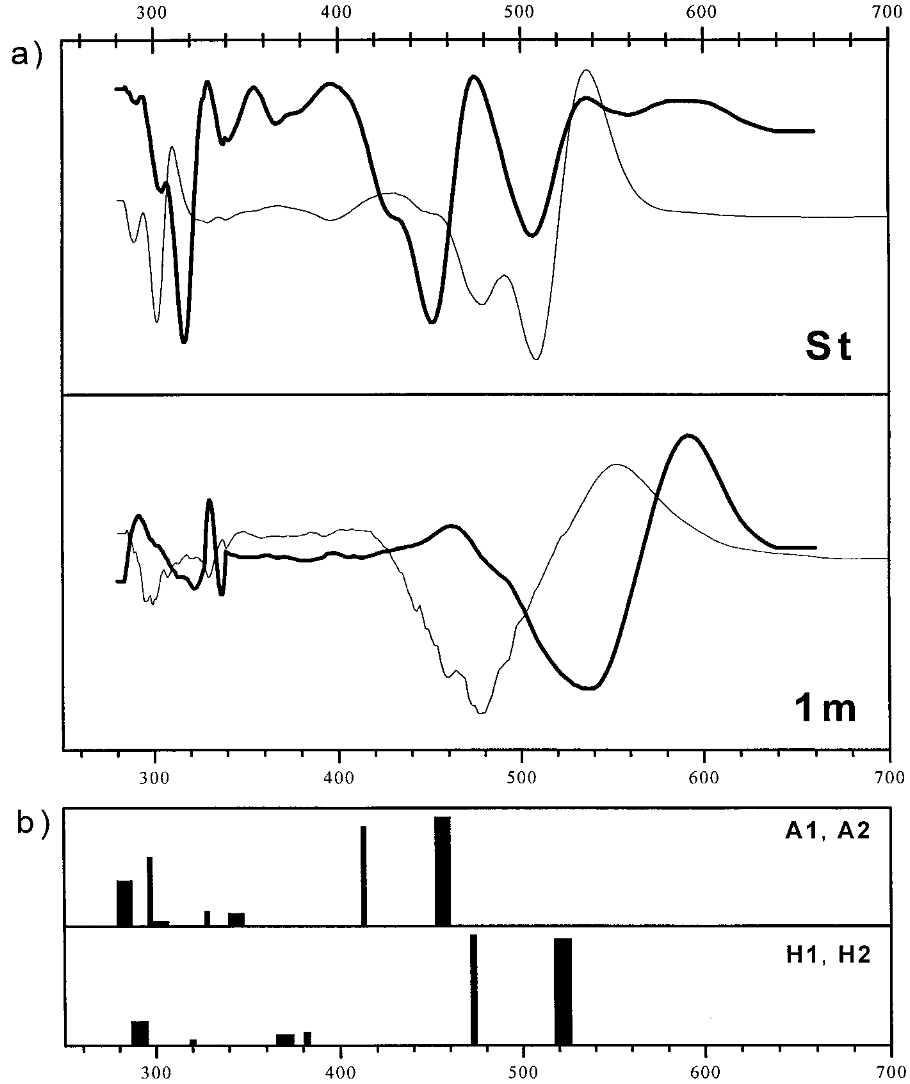


Fig. 3. (a) Differential spectra of dyes **St** and **1m** in solutions at pH = 13.36 (— A_2, H_2) and pH = 6.82 (— , A_1, H_1), and (b) positions of absorption maxima calculated by the PPP-MO method (A_1, A_2, H_1, H_2).

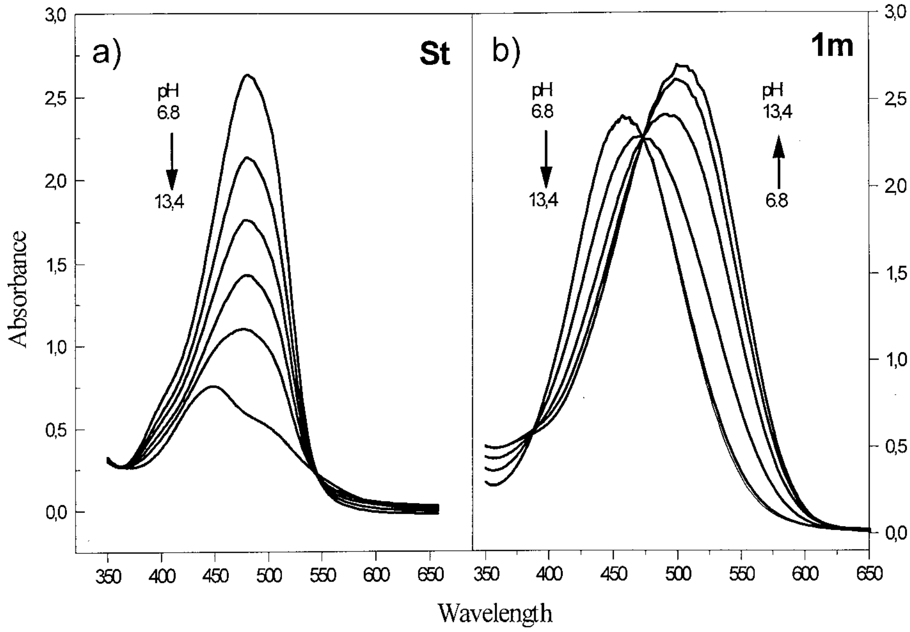


Fig. 4. Examples of changes in the spectral characteristics of dyes **St** and **1m** in solutions at various pH values.

groups according to the relationships known in the literature [2].

3.3. Dyes' pK_a values

Knowing the values of pK_a of the dyes, one can assess the sensitivity of the examined structures to alkaline agents, which is of importance in determining the dye fastness to washing.

The determination of pK_a values for dyes **1o–p** was possible since these dyes appear, in a strongly alkaline medium, only in the hydrazone form ionised at the imine nitrogen atom [26]). Such a determination cannot be performed for dye **St** in which other types of equilibrium and the lack of the form $\mathbf{H_2}$ is observed (Figs. 3 and 4a).

Dye **St** exists in a very stable hydrazone form $\mathbf{H_1}$, even in a solution of pH = 13.36. This form is sufficiently stable so that the dye is not completely converted into the ionised azo form $\mathbf{A_2}$ existing with small quantities of the hydrazone form $\mathbf{H_1}$, which is shown by differential spectra of absorption bands (Fig. 3a). Analogous measurements of dyes **1o–p** show that these dyes occur only in the hydrazone form $\mathbf{H_1}$ at pH = 6.82 and in the anionic hydrazone form $\mathbf{H_2}$ at pH = 13.36.

The determined values of pK_a [2,27] are shown in Table 2.

The low acidity of isomer **1o** compared to **1p** probably results from stabilisation of the intermolecular system by interaction of ionised group -SO_3^-, and the formation of a 6-membered ring with intermolecular hydrogen bonding [28,29]. Dyes **1o–p** occur only in the hydrazone form, and the presence of azo forms cannot be detected even by means of the analysis of second order spectra (Fig. 3).

Table 2
Determined values of pK_a for dyes **1o–p** and **St**

Dye	**1o**	**1m**	**1p**	**St**[a]
pK_a	9.76	9.18	9.34	12.91
r	0.975	0.974	0.992	0.978

[a] Azo form $\mathbf{A_2}$, r-correlation coefficient.

The most acidic dye is **1m**, in which no direct conjugation occurs between the imine nitrogen atom and the ionised sulphonic group in the ionised form.

Analysis of the **1o** and **St** spectra shows also that the change of substituent position in analogous chromophore systems does not always lead to expected colour effects and performance properties of dyes. These facts would explain the origin of the observed differences in colour and performance properties of dyes mentioned in our previous paper [1]. In dye **St**, the sulphonic group strongly stabilises the hydrazone form, and this dye is ionised in the azo form, unlike dyes **1o**, **1m** and **1p**, which are ionised in the hydrazone forms.

In order to determine possible factors affecting the properties of the dyes, their structure was studied using quantum-chemical methods such as PPP-MO and AM1.

3.4. Calculation of the electronic structure of dyes by the PPP-MO and AM1 methods

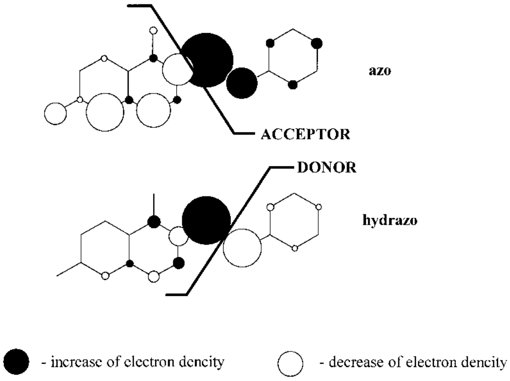
In order to ascribe particular bands to appropriate forms of the dyes, the basic positions of the azo and hydrazone forms, as well as the changes in the molecule electronic density in the excited state, were calculated by the PPP-MO method. Nine configurations, including three engaged and three unengaged scf-mo's, were taken into account. Using ideal geometry with bond angles 120°, two-centre repulsion integrals were calculated according to Mataga–Nishimoto's formula [30]. The same set of input data was used for the calculation for the standard dye **St** and for dyes **1o–p**. In accordance with accepted views [4–8] the sulphonic group does not affect the conjugated system, irrespective of the substitution position in either the naphthalene or phenyl ring.

Comparing the results of calculations (Table 3) with experimental data (Table 1), it was found that the position of bands can be well foreseen by calculation with the quantum-chemical PPP-MO method using standard parameters. The difference between the calculated and found values was only −3–+8 nm. The calculated value of λ_{max} for the azo form was 413 nm in the standard dye, which indicates that dye **St** occurs only in the hydrazone form. The existence of this form is not found even in the second order spectra.

Second order spectra analysis did not show bands corresponding to the azo form in dyes **1o–p** (Table 3), which indicates that these dyes (**1o–p**) occur only in the hydrazone form.

Changes in electronic density calculated by the PPP method show that, in the hydrazone form, the highest changes in electronic density take place in the naphthalene ring, and therefore the substituents present there have the highest effect on the colour of the dye [33]).

The distribution of electronic density in the excited state of the azo and hydrazone forms points to changes associated with the π→π* transition.



The calculated distribution of electronic density in the excited state of the azo and hydrazone forms is similar to that cited in reports on similar compounds [30–33].

Changes in the electronic density are relatively low at the carbon atoms to which the sulphonic group is substituted, viz. 3- in the naphthalene ring (J acid), as well as 2′, 3′ and 4′ in the phenyl ring. It follows from the calculations that the

Table 3
Spectral characteristic of the phenyl-*o*-hydroxyazo chromophore system (**St** and **1o,m,p**) calculated by the PPP-MO method

Form	A_1	A_2	H_1	H_2
λ_{max} (calc)	413	456	473	522

Table 4
Changes in angles α and β and the calculated values of bond length of dyes **St** and **1**

	Azo				Hydrazo			
Dye	α [°]	β [°]	–C–N=	–N=N–	α [°]	β [°]	–C=N–	=N–N–
St	1.9	−121.6	1.424	1.232	−3.9	124.7	1.332	1.297
1o	54.6	116.6	1.480	1.272	−27.2	124.1	1.325	1.312
1m	75.4	120.6	1.426	1.229	4.0	123.8	1.329	1.306
1p	−23.8	121.8	1.428	1.227	−6.7	123.9	1.326	1.311

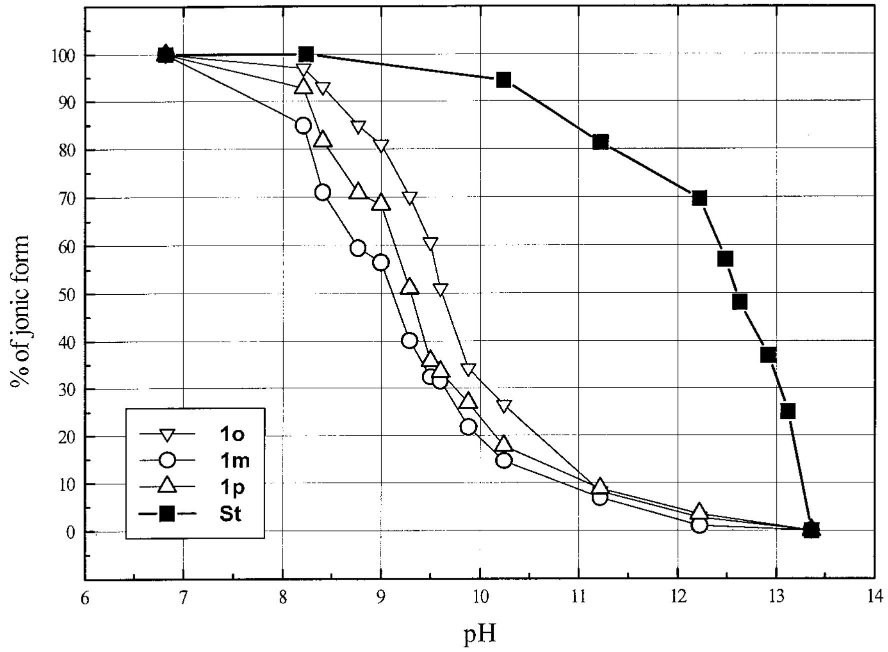


Fig. 5. Content of ionic forms (H_2, A_2) and unionised forms (H_1) in dyes **St**, **1o–p** versus pH: (% A_2 or H_2) = f(pH).

amino group in the hydrazone form interacts with the conjugated system only to a low extent, and hence has a low effect resulting from phosgene treatment on the colour of urea dyes [3].

The calculated values of λ_{max} are similar to those determined by the spectrophotometric method. Differences result from the electronic effects of the sulphonic group in the diazo component in the phenyl ring; the highest are observed in dyes **1o** and **1p** for the form H_2, i.e. where no steric effects are present. Dyes **St** and **1o** absorb within the range shifted towards shorter wavelengths. This band shift may be ascribed to additional intramolecular stabilisation contributed to by the sulphonic groups (Table 1).

The PPP-MO method does not provide information about the actual spatial structure of a molecule. It is assumed in this method that the molecule is flat (maximum conjugation effect), while the bond rotation effect may be taken into account only by an arbitrary correction of input data. In order to explain the causes of observed colour effects, we have utilised the more time-consuming AM1 method and that of molecular

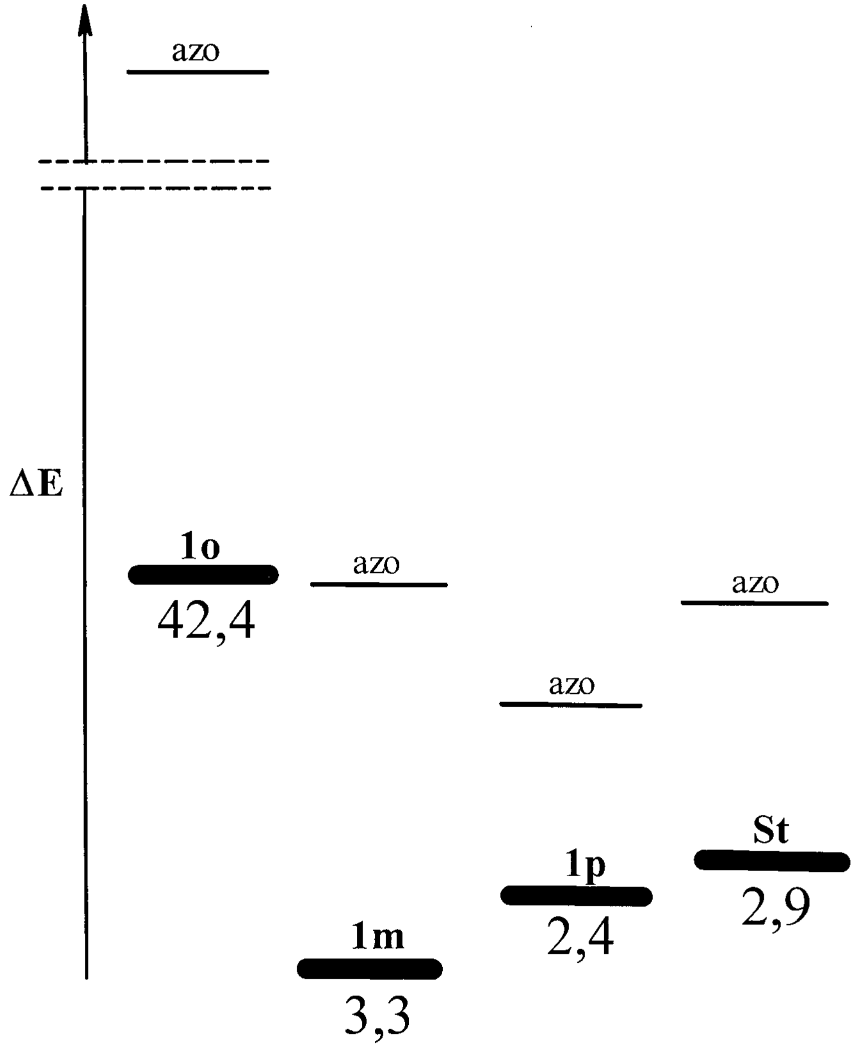
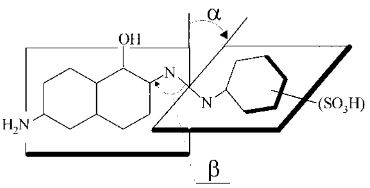


Fig. 6. Differences in the formation energy of azo and hydrazone forms of dyes **St** and **1** [kcal/mol].

dynamics, which allows us to obtain a more real molecule spatial image [3,8,34].

To optimise the dye molecule geometry, the force field (FF) and MO methods were used [34]. Calculations were made for dyes in the azo and hydrazone forms (Fig. 3b, Table 3). Comparison with experimental data (Table 1) confirms the assumption that the observed differences in the spectral properties of the dye under investigation are due to spatial factors. Changes in the angle between the planes of the naphthalene and phenyl rings (angle α), and that in the bond angle C-N(azo)-N (angle β), were used as assessment criterion.



The results obtained are shown in Table 4 and Fig. 6. According to literature data, differences in the energy values of forms $\mathbf{A_1}$ and $\mathbf{H_1}$ for 2-phenylazo-1-naphthol calculated by the AM1 method amount to 2.20 kcal/mol [25], and are similar to those calculated for the dyes under investigation. Similarly, calculated values of the bond lengths of dyes **St** and **1o–p** are similar to those determined by X-ray and neutron diffraction methods. These experimentally found values for 2-phenylazo-1-naphthol are as follows: –N = N– 1.233–1.255, C_{ar}–N = 1.431, = N–N– 1.295–1.308 [35,36], –C = N– 1.343–1.338 [37]). The agreement between the calculated values and the literature data indicates that the examined dyes in the hydrazone form $\mathbf{H_1}$ have almost a flat structure, in which the phenyl ring is deflected from the naphthalene ring plane by $+4 \div -6.7°$. Only in dye **1o** is this angle considerably higher i.e. to 27.2°. This results in decreased conjugation with the naphthalene ring and a low acidity of the imine hydrogen atom of form $\mathbf{H_1}$. The observed effect clearly indicates the role of the sulphonic group, and its effect on the properties of *o*-hydroxyazo dyes due to which these dyes have different properties to those of derivatives containing no sulphonic groups [14,35,38].

From the performed calculations, it follows that the hydrazone form is more stable, although the energy differences are negligible. This form is, however, more preferential, being flat and because of this, conjugation in the phenylazonaphthalene system is more effective. An exception is isomer *ortho*-(**1o**), in which the forced rotation angle of the phenyl ring in relation to the naphthalene ring α is as high as −27.2°. This is the cause of the hypsochromic effect observed in dye **1o**. The calculated value of the rotation angle was introduced to the calculation data in the PPP-MO method in order to correct the value of the resonance integral of the bond –NH–C(ar), according to the relationship [4,38]:

$$\beta_{mn} = \beta^{o}_{mn} \times \cos\alpha$$

Only when the deflection from planarity was taken into account, the obtained value of $\lambda_{\max}$ was 463 nm for the hydrazone form $\mathbf{H_1}$ of dye **1o**, being different from that found experimentally only by 2 nm. The agreement of the calculated values is very high, despite the fact that the possibility of the effect of solvent on the spectrum was not taken into account in the calculations.

4. Conclusions

The colour parameters of monoazo dyes, analogues of C.I. Direct Red 23 (CI 291160) containing sulphonic groups in the diazo component have been examined; it was found that the position of the sulphonic group affected the colour and properties of the dyes. It was assumed that the sulphonic group not only affects dye solubility, but it also plays a substituent role which affects the spatial structure of the dye molecules. By forcing rotation of the phenyl ring in relation to the naphthalene ring, it may affect the colour of the dyes.

In order to verify this, values of the pK_a of the imine groups in isomeric dyes were determined. Analysis of changes in the spectral characteristics in solutions of various pH values together with the results of calculations by PPP-MO and AM1 methods, made it possible to deduce reasons for the observed differences in the colour of dyes **St**, **1o**, **1m**, **1p**.

To calculate the value of $\lambda_{\max}$, the PPP-MO method was used (Table 2), taking into account the deflection from the flat system calculated by the AM1 method. In all the examined cases, changes in angles α and β were observed. The results of these calculations are consistent with those found experimentally. It was found that the dye spatial structure is mainly affected by the sulphonic group in a position *ortho*- in relation to the azo bond in dye **1o**. This is shown both by the highest changes both in the total molecule energy and the obtuse angle of the azo bond β (–C–N = N–). Corresponding changes in the other dyes are smaller. The differences in the position of $\lambda_{\max}$ of cotton fabric dyed with particular dyes can be accounted for by the different spatial structure of isomeric compounds [1].

It has been found that the sulphonic group in position *ortho*- to the azo bond stabilises the dye hydrazone form particularly when the molecule structure allows for free rotation around the bond –C(ar)–N– as it is in dye **St**.

The presence of a sulphonic group in the naphthalene ring does not cause analogous changes, but influences the dye resistance to alkaline medium (Fig. 5 and text). As a consequence of these observations, it is understandable that derivatives of J acid are widely used as direct urea dyes, and that replacement of them with isomeric dyes containing a sulphonic acid group in the phenyl ring is not viable.

The results obtained indicate that the sulphonic group is a substituent which should be taken into account in the calculation parameters, although it has not been previously mentioned. It has been also found that combination of molecular dynamics method, AM1 and PPP-MO, makes it possible to foresee more precisely the spatial structure of dyes, and at the same time to correct the input data for calculations by the PPP method in such a way that the obtained values of $\lambda_{\max}$ become closer to the absorption bands determined experimentally.

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