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ScienceDirect
Dyes and Pigments 75 (2007) 45–51
DYES and PIGMENTS
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The research of the azo–hydrazone equilibrium by means of AM1 method based on the example of an azo dye – the Schäffer salt derivative

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Received 7 April 2006; received in revised form 5 May 2006; accepted 8 May 2006
Available online 11 July 2006

Abstract

An AM1 and ZINDO/S method, azo–hydrazone equilibrium of an azo dye (Schäffer acid derivative) and a model dye (2-naphthol derivative) were examined by means of quantum-chemical methods of calculations. Calculations performed for an isolated molecule (in vacuum) evidenced a higher stability of an azo form [A]. Hydration of dye molecule shows that a hydrazone form [H] is more stable in water solution. These researches confirm practical conclusions about the superiority or the exclusive occurrence of dyes in hydrazone form in real structures of *o*-hydroxyazo dyes.

Keywords: Azo dyes; Schäffer salt; Azo–hydrazone equilibrium; AM1; Quantum-chemical calculations

1. Introduction

Most of the azo dyes occur in a state of equilibrium of two tautomeric forms: an azo [A] and a hydrazone [H] form. Their mutual proportions depend on series of factors, among which the most important are the kind of substituents (donors (E_D) or acceptors (E_A)) and the kind of solvents used for investigations. Spectral analysis allows determining the general proportions of [A]/[H] form, however, the lack of knowledge of extinction coefficient (ε_{max}) of [A] and [H] form, makes the determination of the precise value of the equilibrium constant (K_T) impossible. Its knowledge has an important meaning in industry practice because about 92% of monoazo dyes published in Colour Index show the existence of such equilibrium [1].

The equilibrium of [A]/[H] of naphthol derivatives was observed over 100 years ago and has been explained by means of existence of a ‘‘movable’’ proton in the molecule. The fact that neither [A] form nor [H] form can be separated, gives an evidence of a low barrier of double bond transition. These changes slightly change the chemical structure, but they considerably influence on the changes of dipole moment values [2–6].

It was observed that there are two factors which decide on the position of the equilibrium state [A/H], in particular [3,4]:

- selective solvation depending on the structure of the solvent, and
- an ability of the solvent to form stronger intermolecular hydrogen bonds with a particular tautomeric form.

In our research we are interested in acid dyes, derivatives of Schäffer salt derivatives, possessing the two ‘‘reactive’’ centres, which determine the state of equilibrium [A]/[H] (Fig. 1).

A 2-naphthol derivative was used, as a model compound, for comparative purposes [2].

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0143-7208/$ - see front matter
doi:10.1016/j.dyepig.2006.05.016

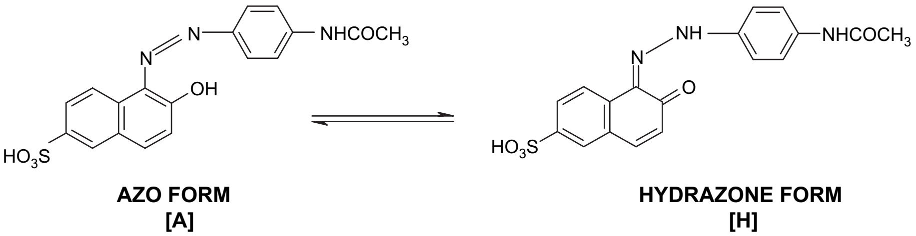


Fig. 1. Azo–hydrazone equilibrium of Schäffer acid derivative.

2. Experimental

Quantum-chemical calculations were performed by means of the AM1 method for both [A] and [H] forms of the dye in gaseous phase and in water (HyperChem v. 5.02 program). Optimization of geometric structure was performed by means MM+ and AM1 method until constant energy of the molecule was obtained [7,8] (when calculating we took the fact of ionization of the sulfo group under consideration). Values of HOMO and LUMO energies were calculated with the use of a ZINDO/S method.

Energy of stabilization of the hydrated form of the dye (ΔE_{dye}) was calculated using Eq. (1):

$$\Delta E_{\text{dye}} = E_{\text{dye-solv}} - n \times E_{\text{solv}} \qquad (1)$$

where:

$E_{\text{dye-solv}}$ – energy of the dye solvation [kcal/mol]
E_{solv} – energy of solvent solvation ($E_{\text{solv}} = -59.266$ kcal/mol for water)
n – number of water molecules

Relative energy of the tautomer equilibrium stabilization (ΔH_T [kcal/mol]) was determined by means of Eq. (2):

$$\Delta H_T = E_{[A]} - E_{[H]} \qquad (2)$$

where $E_{[A]\ ([H])}$ – energy of stabilization of the azo (hydrazone) form [kcal/mol] and a value of the tautomeric equilibrium constant – K_T [14,15] was determined by means of Eq. (3):

$$\log K_T = -\Delta H_T/2.303RT = -\Delta H_T/1.364 \qquad (3)$$

where:

R – gas constant ($= 8.314\ \text{J} \times \text{K}^{-1}\ \text{mol}^{-1}$)
T – temperature ($= 295$ K).

3. Discussion of results

An attempt to determine an [A]/[H] equilibrium by means of quantum-chemical calculations was undertaken. The main problem is the fact that in these calculations the molecules in vacuum, isolated from another dyes and solvent molecules, are analysed. It is necessary to take into consideration the above factors during the analysis of the real dyes dissolved e.g. in water. Calculations of dyes in vacuum are sufficient for many analyses, but they do not describe correctly interactions in solutions [5].

Under conditions of dye application, in alkaline medium, the change of electron density in groups undergoing ionization, such as sulfo group (it decides about the solubility of dye), occurs. The $-SO_3H$ groups are used in dyes in view of their ability to improve solubility of the compound. They increase the substantivity to cellulose fibre, decrease mutagenicity and they also are good leaving groups in nucleophilic substitution. This group undergoes ionization easily, considerably easier than hydroxy group present in the molecule [9]. This fact should be considered in detail and should be taken into account during calculations of the dye both in its isolated and solvated form. As a result of the carried out experimental research it was stated that the influence of this substituent could not be neglected, because it influences on the physical–chemical properties and fastness to light and alkaline.

At present, the simplified models of interactions between the compound and the solvent are applied, such as the Onsager reaction field model [10] or model of the solvent cage [5]. In calculations, in which the optional quantity of water molecules is taken into consideration, the quantity of possible structures is equal to 4^n (n – number of water molecules), what consequently is a cause of considerable calculation problems. In the case of total analysis, all the functional groups present in the dye molecule and their influence on molecule solvation should be considered.

In our calculation, we have concentrated on the interactions between molecules of solvent and "reactive" centres of a molecule of dye, which are sensitive as regards changes of environment, i.e. an azo ($-N{=}N-$) and hydroxyl ($-OH$) group in [A] form as well as hydrazone ($=N-NH-$) and ketone ($=O$) group in [H] form (Fig. 2) when assuming that the remaining molecules of solvent create a continuous medium of uniform dielectric constant. It was stated that model, in which only two water molecules are considered, sufficiently well describes the [A]/[H] equilibrium of a dye derivative of 2-naphthol [5].

Analysis of the spatial structure of a dye was performed by means of analysis of angles, where the interaction between functional groups or aromatic rings is found to be the lowest (Fig. 3). Calculations were performed by means of molecular mechanics method – MM+ method. This procedure is especially effective in compound with a complicated structure. As a result of calculations it was stated that a position of the acetylamino group is of the basic meaning, for which

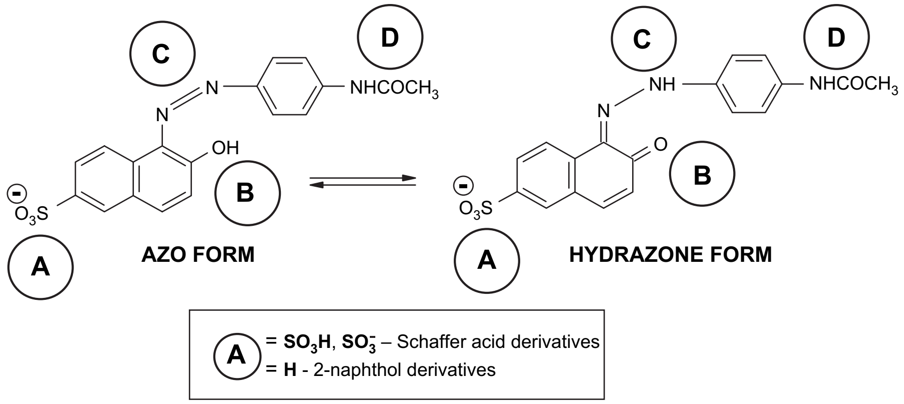


Fig. 2. Places of attaching of water molecules (A, B, C, D).

a gradient of energy of rotation ΔE ($= E_{\max} - E_{\min}$) amounts about 100 kcal/mol (bond a). Analogously, the value of energy of phenyl ring rotation (bond b) is about 26 kcal/mol, but the sulfo group – only about 0.15 kcal/mol (bond c). Next, by means of the AM1 and molecular dynamics method, the structure of the compound was optimised until constant energy of the molecule was obtained.

In our research, we assumed that the sulfo group plays a certain role in contribution of an electron density distribution in molecule and it could have an influence on its solvation. Therefore, we calculated the distribution of electron density in groups: sulfo ($-SO_3H$ or SO_3-), carbonyl (C=O), azo (N=N), hydrazone (=N–NH–), ketone (=O), and hydroxy (–OH). The quantity of negative charge will determine the sequence of attaching of water molecule to the molecule of dye and it could influence on the charges of electron density in non-solvated part of dye. Ionization of the sulfo group causes the change of electron density, not only on itself, but also in the whole molecule of the dye (Fig. 4), whereas it does not cause a change in their array. This sequence is the same for isolated and ionized molecule:

$$A > D > B > C$$

The presented results of calculations show (Fig. 4) that the quantity of negative charge in sulfo group increases in a dye in ionized form (anion). The quantity of the charge in the peripheral acetylamino group undergoes the change, too. The charge in groups: azo ([A] form) or hydrazo ([H] form) and hydroxy ([A] form) or ketone ([H] form) undergoes insignificant change. In real conditions, i.e. a dye in dissolved form, we should consider effects of solvation according to the presented sequence resulting from the value of negative charge on the particular functional groups. Analogical calculations performed for 2-naphthol derivative lead to identical conclusions (Fig. 5).

The illustration of an influence of both the sulfo group and its ionization on the properties of dye is its hardness η – a value determining the stability of the compound i.e. its aromatic character and consequently its stability [11,12]. The bigger this value the stronger is the aromatic nature of the compound and it is more stable. According to the molecular orbital theory, hardness η can be defined as follows:

$$\eta = \frac{[E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}]}{2}$$

which can be estimated using the results from the quantum-chemical calculations. In our investigations, for these

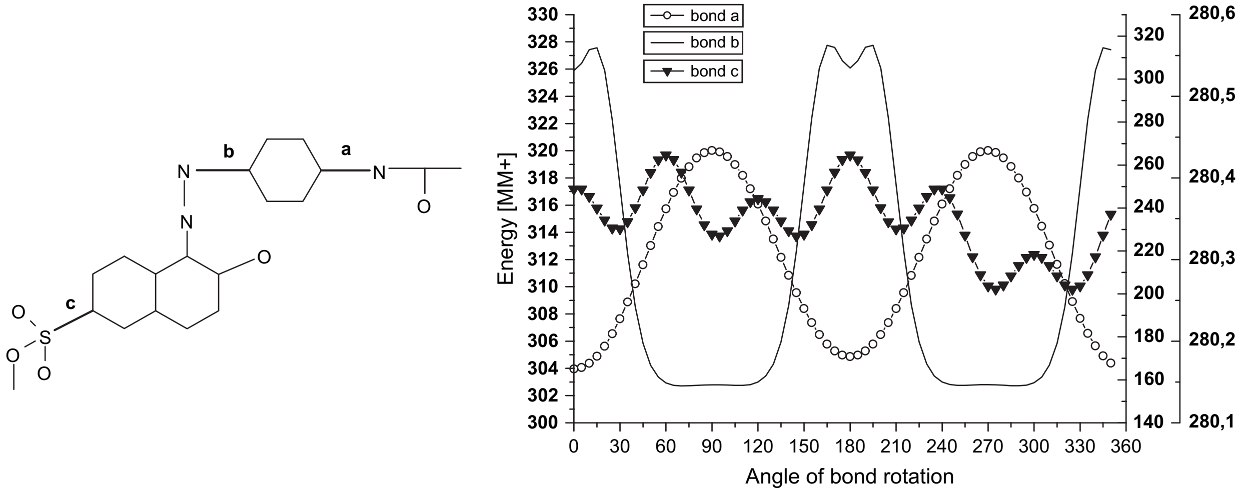


Fig. 3. Energetic barrier of rotation around bonds a, b and c in [A] and [H] forms of a dye. The left scale apply to b bond, right – to a and c bonds. An optimization was performed by means of the MM+ method.

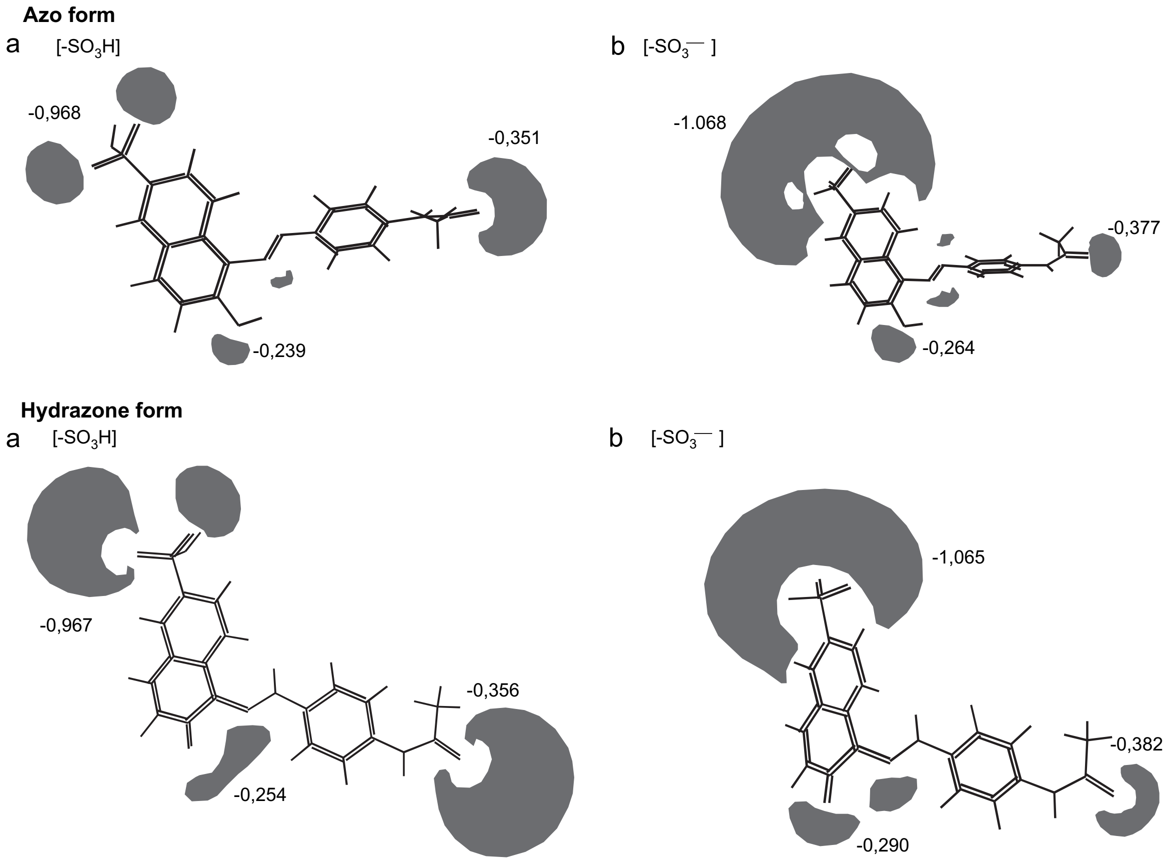


Fig. 4. Distribution of the negative charge on sulfo, azo, hydrazone, hydroxy and ketone groups in [A] and [H] forms of dye.

purposes, we used ZINDO/S method about parameterization adapted to spectral characteristic calculations.

As a result of ionization, the electron densities undergo significant change what entails changes of HOMO and LUMO energy values and consequently changes of the position of absorption bands λ_{max}. These changes are very well reflected by the ZINDO/S method, although sometimes absolute values differ even considerably from the real values [9] (Table 1).

The carried out calculations show that [A] and [H] are nonplanar. In the [A] form the phenyl ring (in relation to −N=N− bond plane) is twisted of to −13.6°, whereas the naphthyl ring is twisted of to 29.4°; in the hydrazone form, respectively, 11.9°, and −1.1°. It results in the fact that ionization of sulfo group influences also on both the change of electron density and on the change of spatial structure of a dye (Table 1). The results of calculations are very approximate or corresponding to X-ray data [13].

The high η value testifies of a shift of equilibrium state towards the azo form of $\eta_{[A]} = 3.260$ (in the case of hydrazone form $\eta_{[H]} = 3.103$), while the ionization of the sulfo group leads to the shift of equilibrium towards the hydrazone form, for which $\eta_{[H]} = 2.855$ ($\eta_{[A]} = 2.712$). Dye molecules without the sulfo group (2-naphthol derivatives) are more stable in the azo form ($\eta_{[A]} = 3.335$, $\eta_{[H]} = 3.108$) and only hydration essentially changes the state of equilibrium. In quantum-chemical calculations the compound is treated as system isolated from interactions with solvent molecules and another molecules of dye. In real conditions only the intermolecular interactions decide about the state of the [A]/[H] equilibrium [14–16]. Such approach to problem causes that there are no systematic dependences between absolute energies of [A] and [H] form and values characteristic for the given solvent.

Literature data obtained based on the spectrophotometric research of dye solutions show that derivatives of naphthols and phenols exist almost exclusively in hydrazone form, whose quantity depends on both the kind of solvent (used for the research) and substituents present in the molecule.

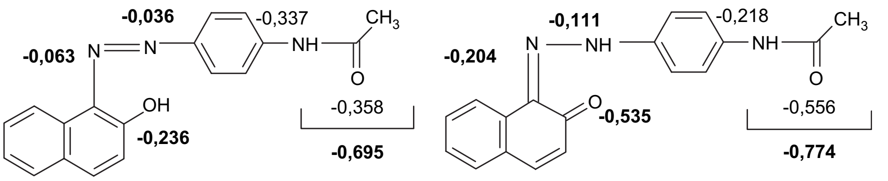
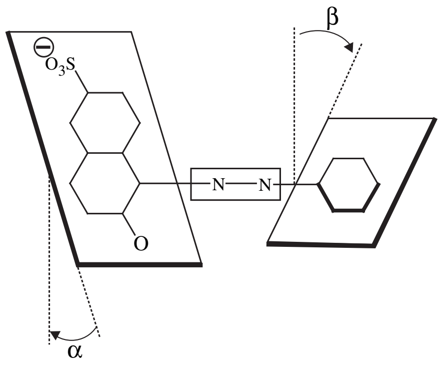


Fig. 5. Distribution of the charge density in azo and hydrazone forms of the model dye, 2-naphthol derivative.

Table 1
Hardness (η) of [A] and [H] forms and value of angles of twist of aromatic rings' planes



No.	Form of dye	ZINDO/S				N═N ↔ Ph, α [°]	N═N ↔ Naph, β [°]
		LUMO	HOMO	η	λ_{max}		
1	[H] [SO_3H]	−1.884	−8.089	3.103	366.5	11.9	−1.1
2	[H] [SO_3^-]	0.744	−4.965	2.855	316.5	−37.2	4.1
3	[A] [SO_3H]	−1.574	−8.093	3.260	370.2	−13.6	29.4
4	[A] [SO_3^-]	0.753	−4.671	2.712	343.9	−38.0	−34.3

These quantities oscillate from 10% to 100%, which means that in many cases, the azo–hydrazone equilibrium decides the properties of dyes [3–6,14–19], however, there was no relation observed between K_T and dielectric constant of the solvent [5,20–22].

Then, we carried out calculations of hydrated molecules of dye, optimising their geometric structure by means of the AM1 method, until the constant value of energy was obtained.

The analysis of the change of energy of hydration shows that the sulfo group undergoes hydration (ionization) as the first; the following groups are an oxygen atom, nitrogen atom and an acetyl group (Fig. 6). For both the derivative of Schäffer acid and 2-naphthol, the first molecule of water is attached to the place of the higher negative charge, which additionally stabilizes the azo form, while connection of the next molecules of water shifts this equilibrium towards formation of more stable, hydrated [H] form (Table 2).

Table 2
Values of creating energy of [A] and [H] forms of dyes (Schäffer acid derivatives): **1**,**3** (in acid form), **2**,**4** (in ionized form) and **2**,**6** (2-naphthol derivatives)

No.	Form of dye	H_T[kcal/mol]	× nH$_2$O
1	[A_1] [SO_3H]	−79.47	–
2	[A_2] [SO_3^-]	−121.01	−386.57 ($n = 4$)
3	[H_3] [SO_3H]	−69.75	–
4	[H_4] [SO_3^-]	−118.22	−394.00 ($n = 4$)
5	[A_5]	40.46	−150.29 ($n = 3$)
6	[H_6]	41.84	−152.08 ($n = 3$)

Furthermore, it was stated that attaching of the two molecules of water to $-SO_3^-$ and −OH groups results in better stabilization of the azo form, but attaching of the two next molecules – stabilizes the hydrazone form more, however, attaching to the ═N–NH– group is advantageous in comparison to attaching to the carbonyl (═O) group. An order of attachment of the next molecules of water is not consistent with the changes of the charge density, in particular, functional groups. Only hydration of the acetamide group causes the [H] form to become more stable.

Values of the tautomeric equilibrium constant K_T [20,22] show that about 10% of 2-naphthol derivatives occur in vacuum in [H] form, whereas in the case of the dyes derived from Schäffer acid, they occur exclusively in the azo form (±1%).

As it is seen on the basis of the quoted results, the sulfo group and its ionization has generally no influence on the value of the equilibrium constant K_T, or its influence is negligibly small (<1%) (Table 3). Solvation of the dye molecule causes the change of the equilibrium state and molecules occur almost exclusively in the hydrazone form, what is agreeable with the experimental data concerning the dyes, which are the *o*-hydroxyazo derivatives [1].

3.1. Lengths of hydrogen bonds

Intermolecular hydrogen bonds with the suitable functional groups of the dye are formed as a result of hydration. The performed calculations show that a hydrogen bond with the azo or hydrazone group (Tables 4 and 5) and of the highest length has

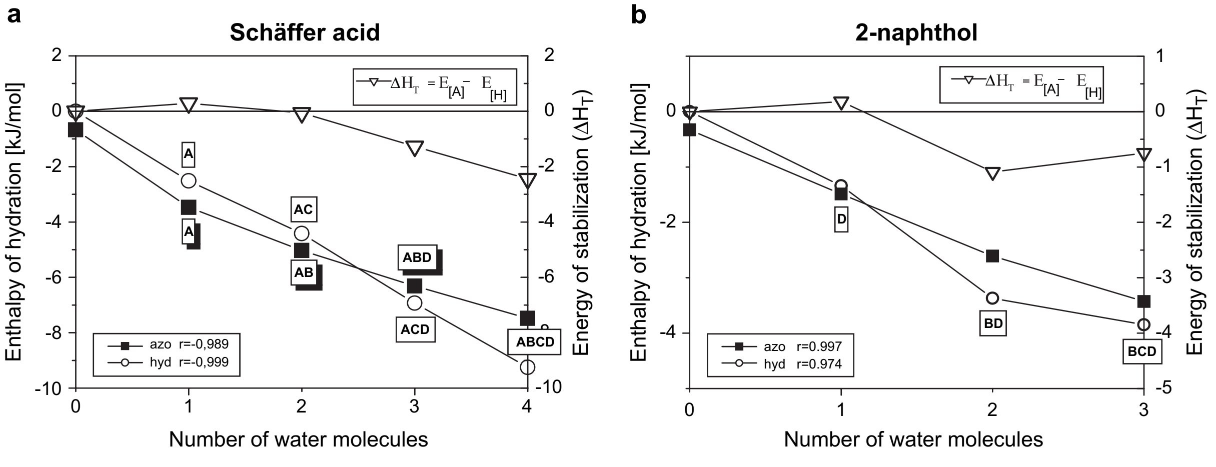


Fig. 6. The energies of hydration and stabilization of the [A] and [H] forms of the dyes, Schäffer acid and 2-naphthol derivatives.

Table 3
Calculated values of the tautomeric equilibrium constant K_T (data in Table 2)

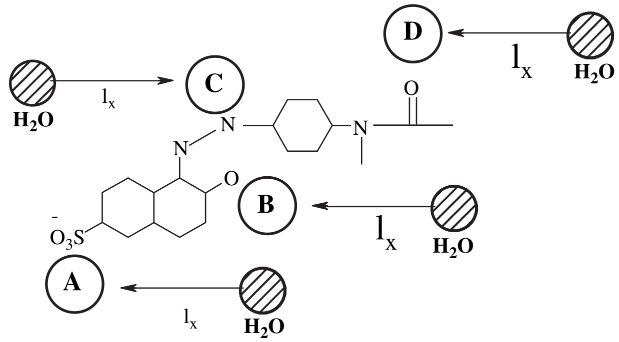
[A]/[H]	K_T	K_T [× nH_2O]
[SO_3H]	1.33×10^8	–
[SO_3^-]	1.11×10^2	3.56×10^{-6}
[H]	10.1	4.8×10^{-2}

the smallest contribution in the energy of stabilization (Table 3). The calculations for 2-naphthol derivative lead to similar conclusions (Table 3). A presence of the sulfo group causes that bonds l_x, particulary hydrogen bonds with [H] tautomer, are insignificantly stronger (shorter) (Tables 4 and 5). The weakest bonds are those with the −N═N− or ═N−NH− group.

4. Conclusions

For the determination of the role of $-SO_3H$ group in molecule and its influence on the equilibrium of azo and hydrazone form, we used the AM1 method, on the assumption of selective solvation of functional group and considering the acetylamino group (−NHAc). The simplified model ignoring the Onsager reaction field model was applied. In our calculations we concentrated only on the hydration of "reactive" centres of dye molecules, where the solvent is viewed as continuous medium of uniform dielectric constant. An order of attaching of the next molecules of water resulted from the calculations of quantity of the negative charge of the optimised structures of dyes. However, contrary to sulfo derivatives, which are very well soluble in water solution, derivatives of 2-naphthol do not show such feature, because they are pigments. We assume that they are sparingly soluble in many organic solvents and especially in water. In water solution they occur in crystalline form, strongly aggregated and consequently weakly solvated.

Table 4
Lengths of hydrogen bonds in solvated molecules of Schäffer acid derivative (A−substituent= SO_3^-)[a]



$n \times H_2O$[b]	l_x [A]	l_x [H]
1	(l_a,l_b,l_d) = 2.11–2.19	(l_a,l_b,l_d) = 2.11–2.19
2	(l_a,l_b,l_d) = 2.11–2.29	(l_a,l_b,l_d) = 2.11–2.19
3	(l_a,l_b,l_d) = 2.11–2.51	(l_a,l_b,l_d) = 2.11–2.19
4	(l_a,l_b,l_d) = 2.10–2.21	(l_a,l_b,l_d) = 2.11–2.19

[a] l_c = 2.79–4.34.
[b] number of water molecules.

Table 5
Lengths of hydrogen bonds in solvated molecules of 2-naphthol derivative (A−substituent= H)[a]

$n \times H_2O$[b]	l_x [A]	l_x [H]
1	(l_b,l_d) = 2.10–2.23	(l_b,l_d) = 2.24
2	(l_b,l_d) = 2.10–2.22	(l_b,l_d) = 2.22–2.27
3	(l_b,l_d) = 2.23	(l_b,l_d) = 2.22–2.25

[a] l_c = 2.74–3.81.
[b] number of water molecules.

It was stated, in quantum-chemical calculations, that presence of sulfo group (similarly as acetoamino group) influences on the state of [A]/[H] equilibrium, in particular, stages of dye molecules' solvation. Intermolecular hydrogen bonds have high energy − they are stable; the bonds with azo or hydrazone group are the weakest. Furthermore, the sulfo group and especially its ionization, influences on the spatial structure of molecule, hence aromatic character of molecule (harness η) and position of λ_{max} ($\Delta E = E_{LUMO} - E_{HOMO}$) undergo a change. Total solvation (hydration), in other words attaching of four or three molecules of water (in 2-naphthol derivatives), totally stabilizes the dye in [H] form and the quantity of [A] form is very small. Such phenomenon confirms results of dipole moment calculations, which are in concert with the experimental data for dyes of the similar structure [12,23].

Acknowledgements

This research work has been financed from the budgetary funds for science in 2005–2006 as research project No. 3 T09B 082 28.

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