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# Ab initio modeling of the solvent influence on the azo-hydrazone tautomerism[†]

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## Abstract

The solvent effect on the azo (*A*) -hydrazone (*H*) tautomeric equilibrium of 1-phenylazo-4-naphthol is modeled by using ab initio quantum-chemical calculations. It was found that in methanol, methylene chloride and water there exists a strong hydrogen bonding between the particular tautomer and solvent, as well as dipole–dipole dye-solvent interactions. The results show that the *H*-form is more stable in water and methylene chloride, while methanol and i-octane stabilize the *A*-form. The calculational results obtained are in very good agreement with the experimental data in these solvents published previously. © 1998 Elsevier Science Ltd. All rights reserved.

*Keywords:* Tautomerism; Azo dyes; Hydrogen bonding; Solvent effect

## 1. Introduction

The azo (*A*)-hydrazone (*H*) tautomerism of the phenylazonaphthols was observed in the case of 1-phenylazo-4-naphthol (**1**) by Zince and Bindenwald [1] over one century ago, and has been explained by the existence of a 'movable' proton in the molecule [2]. Unfortunately, due to the high proton exchange rate, both tautomeric forms cannot be separated experimentally and therefore it was, for some time, impossible to investigate exactly tautomer-solvent interactions [3,4]. Recently, using newly developed methods for the spectrophotometric analysis of tautomeric equilibria [5], the solvent influence on the *A*-*H* tautomerism of some derivatives of **1** were investigated quantitatively and it was found that the tautomeric ratio (defined as tautomeric constant $K_T = [H]/[A]$) increases in the following order: i-octane < DMFA≅ ethanol < DM SO < methanol ≅ ethyl acetate ≅ acetone < acetonit-rile < 50% ethanol/water < $CHCl_3$ < $CH_2Cl_2$ ≅ formamide < water.

This general trend is valid also in the case of the isomeric 1-phenylazo-2-naphthol and 2-phenylazo-1-naphthol, but the solvent effect is not so pronounced because of the stabilizing intramolecular hydrogen bonding [6]. From the above cited results, it is clear that there is no relation between $K_T$ and the dielectric constants of the solvents, suggesting specific interactions.

Since 92% of mono-azo dyes published in the Colour Index [7] are potentially tautomeric characters, and their spectral behavior in solution (determined by the tautomeric ratio) is very relevant to industrial applications, the investigations over the solvent effect on the tautomeric equilibrium position are of present interest as in theoretical as well as in practical aspect.

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Modeling of the solvent effect on the *A*–*H* tautomerism by using quantum-chemical methods is valuable, because it could shed light on the root of the phenomenon. It is worth noting that dye **1** is a very suitable example for such investigations, because the equilibrium is very sensitive to solvent influence due to lack of intramolecular hydrogen bonding.

## 2. Experimental

Quantum-chemical calculations were performed on a Cray C90 supercomputer (Tokyo Institute of

Table 1
Values of the energies of the *H*- and *A*-forms ($HF/6\text{-}31G^{**}$ level) in different solvents calculated according to the Onsager model

| Solvent | $\epsilon$ | $E_{RHF}$ $H$ (a.u.) | $E_{RHF}$ $A$ (a.u.) | $H$–$A$ gap (kcal/mol) | $K_T$ |
|---|---|---|---|---|---|
| Gas phase | | −796.62979 | −796.63223 | 1.531 | – |
| i-octane | 1.96 | −796.63018 | −796.63228 | 1.317 | 0.116[a] |
| $CH_2Cl_2$ | 9.08 | −796.63085 | −796.63236 | 0.947 | 1.570[a] |
| $CH_3OH$ | 32.63 | −796.63106 | −796.63239 | 0.834 | 0.254[a] |
| Water | 80.37 | −796.63111 | −796.63239 | 0.803 | 1.934[b] |

[a] Ref. 5.

[b] Extrapolated value since **1** is not soluble in water, the nearest value is 1.342 for ethanol/water = 20/80%.

Table 2
Solvent influence on the energies ($HF/6\text{-}31G^{**}$ in a.u.) of both tautomeric forms

| Solvent | $n$ | Without dipole field | | | With dipole field | | |
|---|---|---|---|---|---|---|---|
| | | $A$ | $H$ | $H$–$A$ gap (kcal/mol) | $A$ | $H$ | $H$–$A$ gap (kcal/mol) |
| | 0 | −796.63223 | −796.62979 | 1.531 | −796.63239 | −796.63111 | 0.803 |
| Water | 1 | −872.66830 | −872.66437 | 2.466 | −872.67073 | −872.67082 | 0.0568 |
| | 2 | −948.69964 | −948.69908 | 0.351 | −948.70136 | −948.70463 | −2.051 |
| $CH_2Cl_2$ | 0 | −796.63223 | −796.62979 | 1.531 | −796.63236 | −796.63085 | 0.947 |
| | 1 | −1754.62373 | −1754.62326 | 0.294 | −1754.62396 | −1754.62623 | −1.424 |
| $CH_3OH$ | 0 | −796.63223 | −796.62979 | 1.531 | −796.63239 | −796.63106 | 0.834 |
| | 1 | −911.69173 | −911.68816 | 2.240 | −911.69392 | −911.69068 | 2.033 |

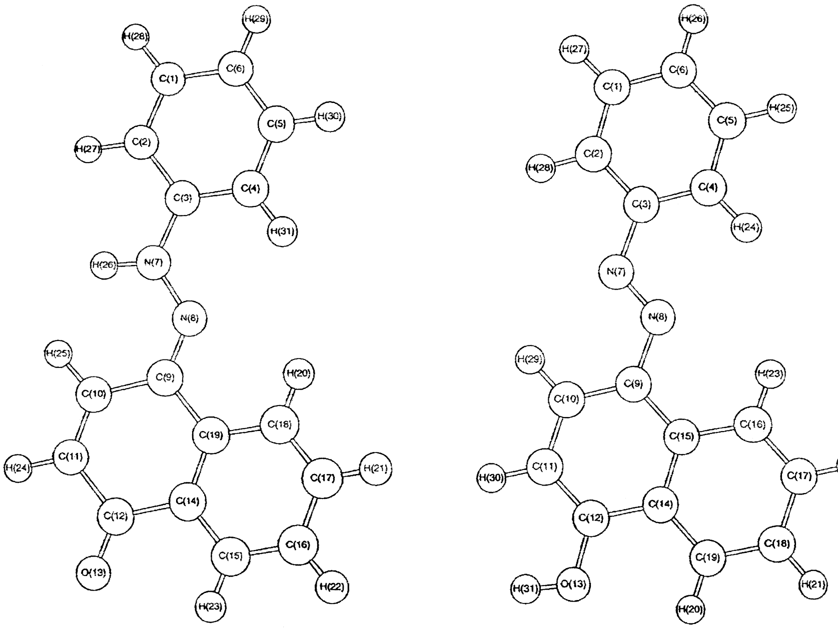

Fig. 1. Schematic presentation of *H*- and *A*-forms of the investigated dye.

Technology) as follows: AM1 method by using Unichem 3.0 (Cray Research Inc.); ab initio calculation ($HF/3-21G$ and $HF/6-31G^{**}$) by using Gaussian'94 [8].

## 3. Results and discussion

Quantum-chemical calculations have usually been carried out in the gas phase, but while gas

Table 3
Solvation energy $\Delta E_s$ (in kcal/mol) of both tautomeric forms in different solvents

| Solvent | *n* | Without dipole field | | | With dipole field | | |
|---|---|---|---|---|---|---|---|
| | | *A* | *H* | *H–A* gap | *A* | *H* | *H–A* gap |
| Water | 1 | 7.819 | 6.884 | −0.935 | 7.059 | 7.919 | 0.86 |
| | 2 | 12.669 | 13.849 | 1.180 | 9.281 | 12.136 | 2.855 |
| $CH_2Cl_2$ | 1 | 2.065 | 3.301 | 1.236 | 1.575 | 3.947 | 2.372 |
| $CH_3OH$ | 1 | 8.026 | 7.317 | −0.709 | 8.333 | 7.135 | −1.198 |

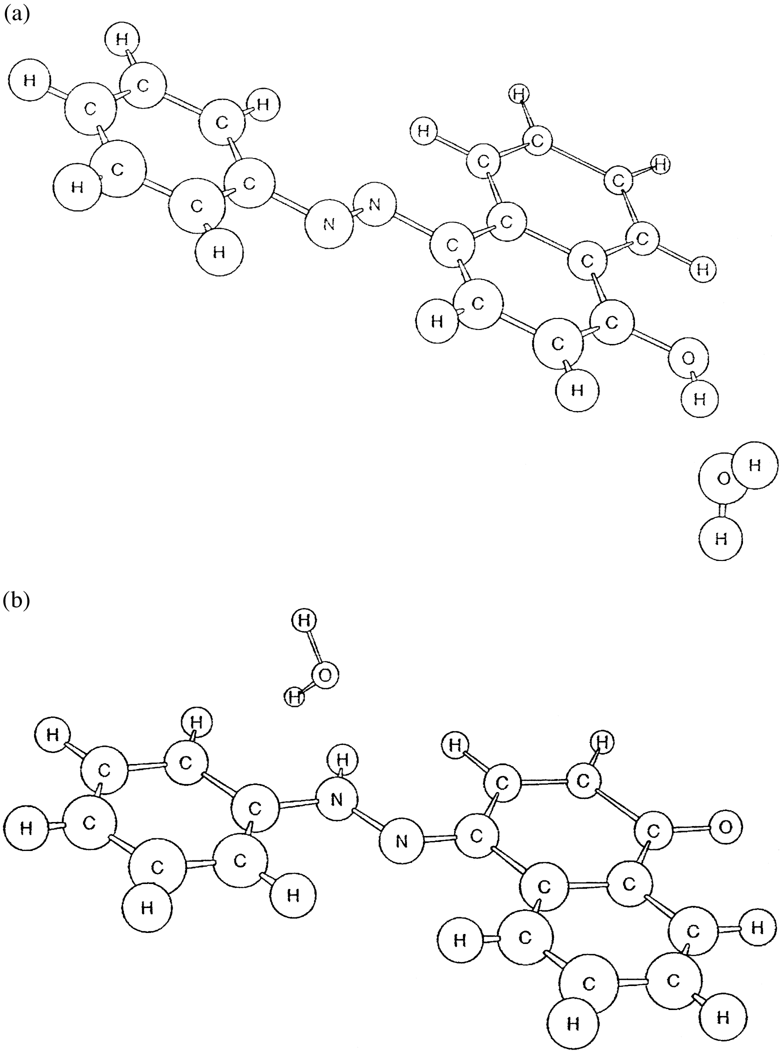

Fig. 2. Interaction of water molecule with *A* (a) and *H* (b) forms.

phase predictions are suitable for many purposes, they are inadequate for describing the *A–H* tautomeric equilibrium in solution, because the properties of the tautomers differs considerably between the gas phase and solution. Dye-solvent interactions were firstly modeled using the Gaussian'94 Onsager reaction field model [9], where the solvent is viewed as a continuous medium of uniform dielectric constant $\epsilon$ and the solvent–solute interaction is the only dipole. The results from such modeling are presented in Table 1.

As can be seen from Table 1, there is no correlation between the relative energies (*H–A* gap) and the tautomeric constants in different solvents, and these calculational results confirm the

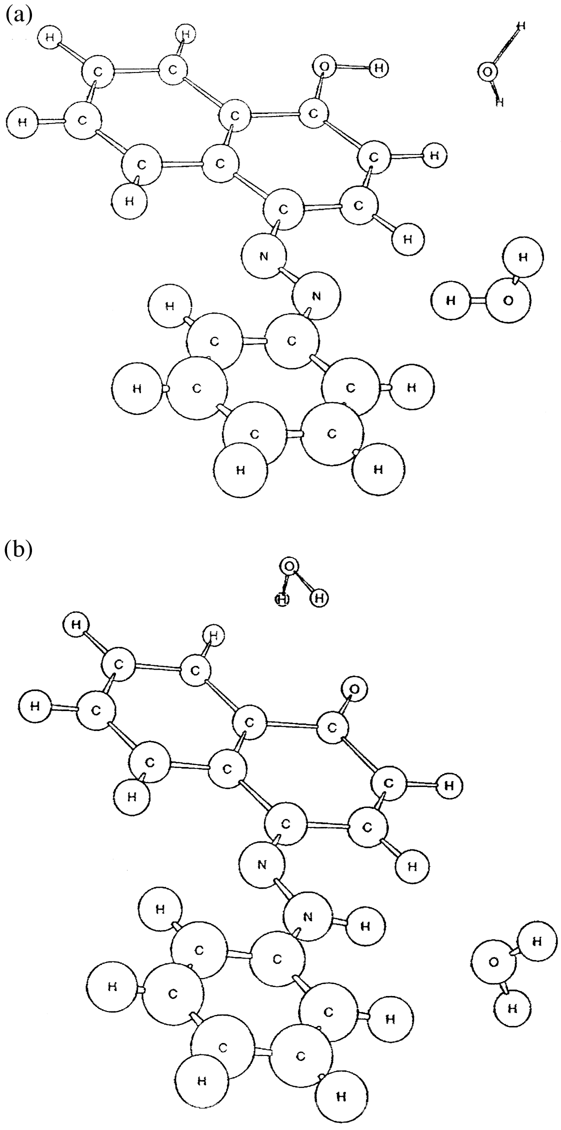

Fig. 3. Interaction of two water molecules with *A* (a) and *H* (b) forms.

experimental fact that the interactions between tautomer and solvent are specific [4–6].

For this reason, further investigations were directed towards modeling of these specific interactions by adding solvent molecules around the molecule of a particular tautomer. There are four possible sites for interaction (and for adding solvent molecule) in each tautomer (Fig. 1). For the *H*-form the possibilities are:

1. O13–C14–H23 plane–interaction with C=O group;
2. O13–C11–H24 plane–interaction with C=O group;
3. H25–H26–H27 plane–interaction with H from N–H group;
4. H20–N8–H31 plane;

and in the case of the A-form:

1. O13–C14–H20 plane–interaction with O from OH group;
2. H31–C12–H30 plane–interaction with H from OH group;
3. H29–N7–H28 plane;
4. H23–N8–H24 plane.

This implies that the number of the variants for each tautomer are $4^n$, where $n$ is the number of solvent molecules added. The large number of possibilities leads to rather extensive computations. Therefore, the initial variants were calculated by using AM1 and $HF/3-21G$ as initial approximations for $HF/6-31G^{**}$ level. Since it is impossible to add endless solvent molecules, the calculations were performed in two ways—only dye–solvent interactions and dye–solvent interactions in the dipole field (Onsager model) in order to take into account the dipole–dipole effect . The solvation energy defined as:

$$\Delta E_s = (E_{\mathrm{RHF-dye}} + n.E_{\mathrm{RHF-solv}}) - E_{\mathrm{RHF-(dye+solv)}}$$

where: $E_{\mathrm{RHF-dye}}$ is the energy of the isolated dye molecule; $E_{\mathrm{RHF-solv}}$ is the energy of the isolated solvent molecule; $E_{\mathrm{RHF-(dye+solv)}}$ is the energy of the interacting dye and solvent molecules; for each of the variants was calculated. In the case of i-octane, because of steric hindrance stable interactions were not found, and most probably in this case only dipole interactions exist. All calculation results are presented in Tables 2 and 3, and Figs. 2–5.

As can be seen from Table 2, and Figs. 2 and 3 in the case of water, in the *A*-form OH...$OH_2$ ($R=1.95$Aů) interaction is preferable, while in the *H*-form NH...$OH_2$ ($R=2.11$Å) interaction

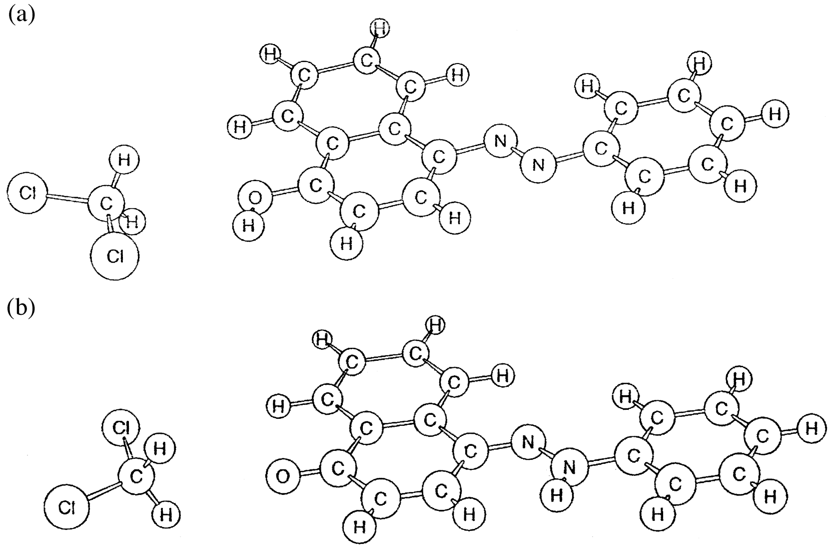

Fig. 4. Interaction of $CH_2Cl_2$ with *A* (a) and *H* (b) forms.

stabilizes more the dye-solvent system. The increase of the number of water molecules leads to a decrease of the H–A gap and stabilization of more of the *H*-form; as indicated by the case of two water molecules, the *H*-form is the more stable. The case of solvent-dye interaction and Onsager model filed together is more reliable, because the calculations of some variants with three molecules water showed that the third molecule does not interact directly with the dye molecule, but influences by interaction with one of the already associated water molecules. The dependence between the *H–A* gap and the number of associated water molecules is shown on Fig. 6. Most probably increase of the number of water molecules above 2 will lead to not such sharp changes, and finally to saturation, and for this reason we conclude that the system 'dye–2 water molecules' describes satisfactorily the real situation in this solvent.

The $CH_2Cl_2$–dye model (Fig. 4) shows that, in this case, O...$H_2CCl_2$ ($R$ = 2.71Å for the *H*-form and 2.93Å for the *A*-form) interaction is preferable (but with very small interaction forces) in both

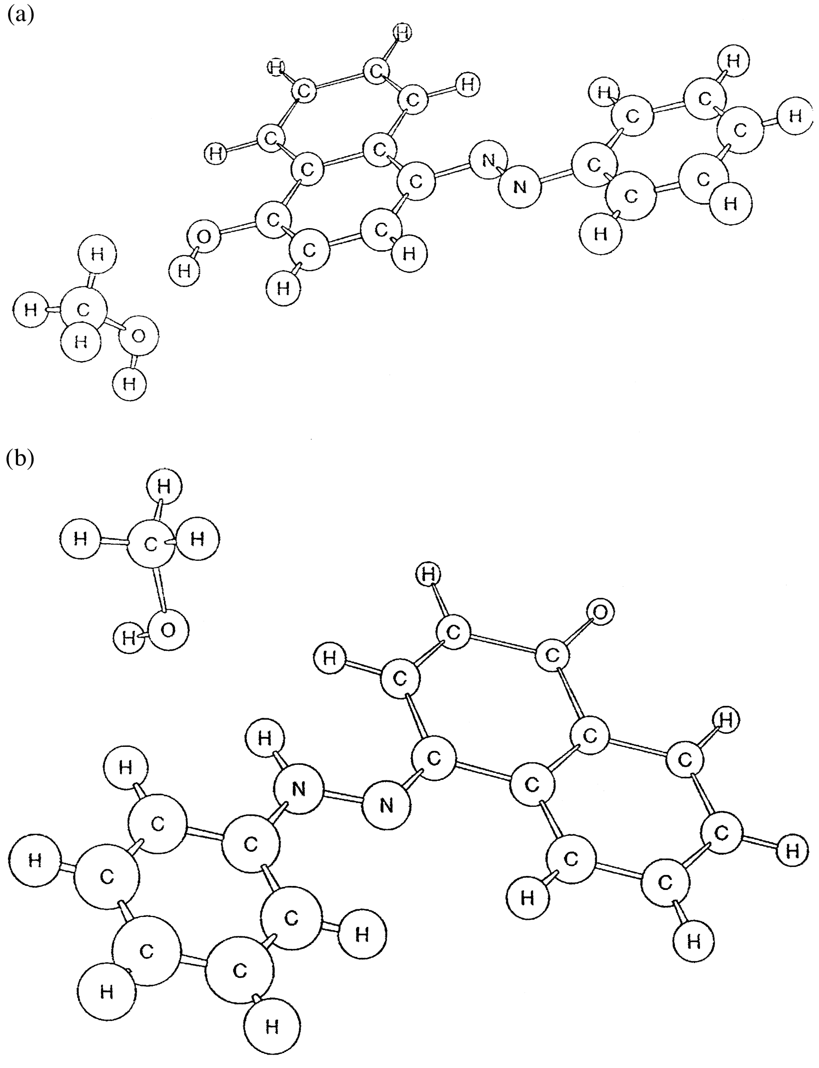

Fig. 5. Interaction of methanol with *A* (a) and *H* (b) forms.

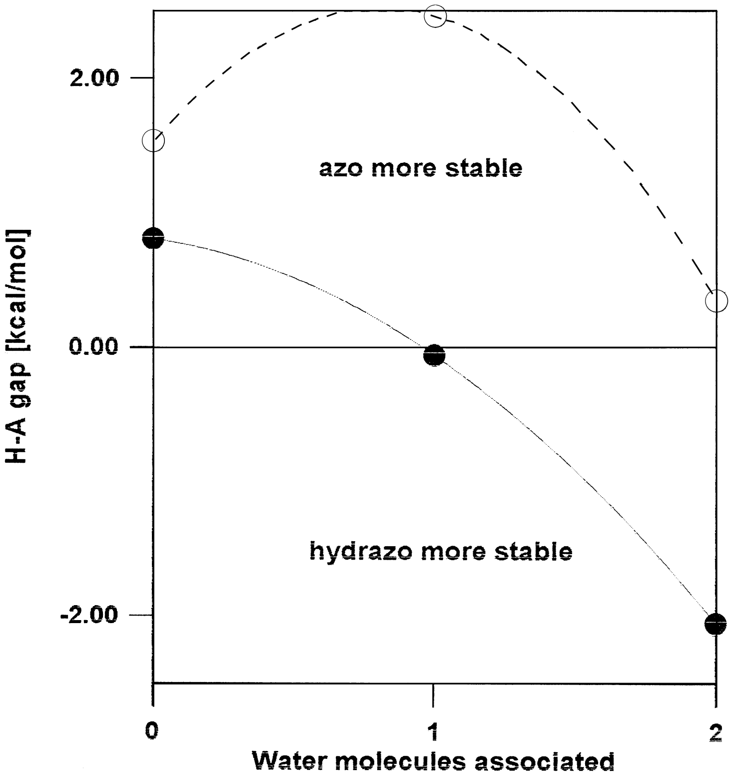

Fig. 6. The change of *H–A* gap as a function of the number of interacting water molecules ( – – – without Onsager field; — with Onsager field).

tautomeric forms, and the *H*-form was found to be more stable. Probably, the addition of more solvent molecules does not significantly change the situation, due to the large steric hindrance factors.

In the case of methanol (Fig. 5) as solvent, the interaction sites are the same as in water, i.e. OH...$OCH_3$ (R = 1.91Å) interaction in the *A*-form and NH...$OCH_3$ (R = 2.20Å) in the *H*-form, but it has been found that the *A*-form is more stable (Tables 2 and 3).

Using the data from Tables 1–3 two excellent correlations (with correlation coefficients more than 0.99) have been found and they are depicted in Fig. 7. Firstly there is correlation between the experimentally obtained tautomeric constants in the four investigated solvents and the energy *H–A* gap in the case of specific interactions in the Onsager field. This correlation shows that the model used realistically describes the situation in solution, and that most probably because of the weak interaction of methanol with the dye, its effect is through dipole interactions. The second correlation between the tautomeric constants and $\Delta E_s$ in the Onsager field shows that the interaction between solvent and dye is most stabilizing for the *H*-form in water and for the *A*-form in methanol, which again is in very good agreement with the experimental results.

From the calculation results and the experimental data [5] it is concluded that two factors are mainly responsible for the position of $K_T$ in different solvents, viz:

1. the solvent ability to form stronger intermolecular hydrogen bonding with a particular tautomeric form;
2. the solute–solvent dipole–dipole interactions.

It must be noted that in the real solution the phenomena are very complicated, and sometimes

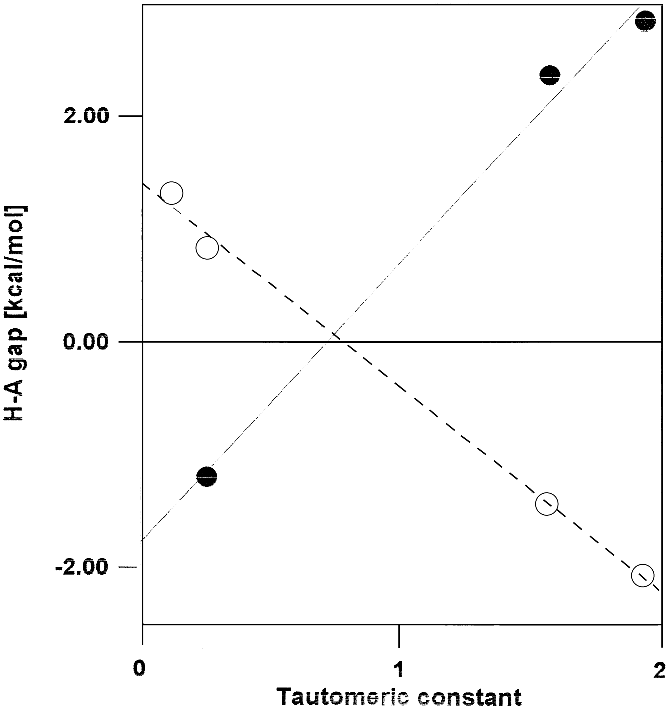

Fig. 7. Correlation between the experimentally obtained tautomeric constants (Table 1) and: *H–A* gap in the $E_{RHF}$ (Table 2 and Table 3; empty circles), and $-\Delta E_s$ (Table 3, filled circles).

impossible to describe, but obviously this simplified model of dye–solvent interaction estimates the real situation with acceptable reliability.

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