

# Relative strength of the intramolecular hydrogen bonding in 1-phenylazo-naphthalen-2-ol and 1-phenyliminomethyl-naphthalen-2-ol

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The relative strength of the intramolecular hydrogen bonding (IHB) in the title compounds has been investigated by means of *ab initio* quantum chemical calculations, UV-Vis spectral study and linear solvation energy relationship analysis (LSER) of the obtained tautomeric constants. It has been found that in acetone (and in all used solvents with substantial proton acceptor abilities) the tautomeric constant in the azonaphthol compound is lower than could be expected. The fact is explained with the breakage of the IHB and the coexistence of closed and open enol tautomers. Copyright © 2008 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

**Keywords:** tautomerism; LSER; spectroscopy; *ab initio*; azonaphthols; Schiff bases; intramolecular hydrogen bonding

## INTRODUCTION

Although the tautomerism in the azonaphthols (1-phenylazo-naphthalene-4-ol, **1**, Scheme 1)<sup>[1]</sup> has been known for more than a century the systematic interpretation of the external factors, affecting the tautomeric equilibrium (solvent effects, temperature, etc.), became reality after developing of advanced chemometric methods for spectral data interpretation.<sup>[2,3]</sup>

Recently, we have investigated systematically the effects of the temperature and solvents on the tautomeric equilibrium in **2** and **3** and their isomers, 2-phenylazo-naphthalen-1-ol and 2-phenyliminomethyl-naphthalen-1-ol,<sup>[4–8]</sup> where an intramolecular hydrogen bonding (IHB) exists. During these studies the tautomeric constants ( $K_T$ ), defined as:

$$K_T = \frac{[K]}{[E]} \quad (1)$$

have been estimated in various solvents.

The solvent effect has been elucidated through linear solvation energy relationship (LSER) analysis of the experimentally obtained tautomeric constants according to the equation:

$$\log K_T = c + s\pi^* + a\alpha + b\beta \quad (2)$$

where  $\pi^*$  describes the effect of the solvent as polar medium;  $\alpha$  and  $\beta$  are measures correspondingly for the solvent proton donor and acceptor abilities;  $c$ ,  $s$ ,  $a$ , and  $b$  are the fitted coefficients (terms) which describe the extent of interaction between the solvent and the solute (the tautomer in this case).

The fitting results have shown that the proton acceptor term ( $b$ ) is zero for the Schiff bases and strongly negative for the corresponding azonaphthols.<sup>[9]</sup> This means that the Schiff bases do not interact with proton acceptor solvents, while such solvents shift the equilibrium toward the enol form (**E**) in the

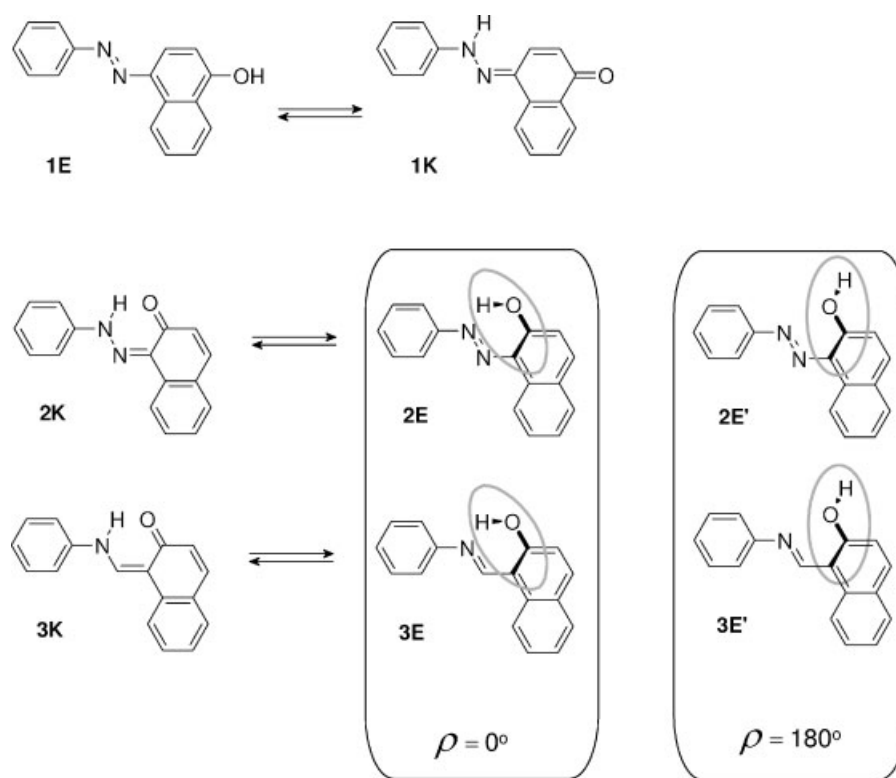
azonaphthols. In addition the statistics of the LSER Eqn (2) in the latter was not good, which has been attributed to the coexistence of two different species in the solution: chelated and nonchelated enol tautomers.<sup>[10]</sup>

Significant differences in the low temperature absorption spectral behavior of **2** and **3** in ethanol and in methylcyclohexane/toluene binary mixture<sup>[4]</sup> have been found as well. While in methylcyclohexane/toluene the tautomeric equilibrium shifts toward the keto form (**K**) with decreasing of the temperature in both compounds, in ethanol such changes can be observed only for **3**. The absorption spectra of **2** in ethanol are virtually temperature independent, which has been explained with a breakage of IHB, because the ethanol is a solvent with commensurable proton acceptor and proton donor abilities. Hence, the tautomeric forms are fixed by the solvent and the tautomeric proton exchange is prevented. The unidirectional spectral changes in both ethanol and methylcyclohexane/toluene in the case of **3** might mean that in this case the IHB is strong enough to resist the specific action of the ethanol.

The gas phase study of the tautomerism of **1–3** and related compounds by electron ionization mass spectrometry<sup>[11]</sup> has shown that the fragmentation of the azonaphthols is very similar to that of **1**, where there is no IHB. On the contrary, the main process in the fragmentation of the corresponding Schiff bases

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**Scheme 1.** Tautomerism in 1–3

has been the loss of the methylene proton from the azomethine group, which leads again to the conclusion that the strength of the IHB is responsible for the lack of further fragmentation.

Therefore the aim of this communication is to attempt an overall explanation of the above described experimental observations in respect of the relative strength of the IHB in **2** and **3**. This has been achieved by *ab initio* quantum chemical calculations and spectral study followed by LSER analysis of the new and existing data.

## EXPERIMENTAL PART

### Synthesis

Compound **2** has been synthesized by a standard coupling reaction of aniline and 2-naphthol,<sup>[12]</sup> recrystallized from ethanol solution and then purified by TLC (chloroform/methanol 95:5).

### Spectroscopy and data processing

The absorption spectra of **2** in three binary solvent compositions (acetone/chloroform, DMSO/diethyl ether, and methanol/water) were recorded on a JASCO V-570 UV-Vis-NIR spectrophotometer equipped with a Julabo ED5 thermostat (precision 1 °C) at room temperature (20 °C) according to the previously described methodology.<sup>[3,5]</sup> The used solvents were of spectral grade.

The recorded spectral datasets with different tautomeric ratios were processed by the Fishing-Net Algorithm, implemented in the MULTIRES software for quantitative analysis of undefined mixtures.<sup>[13]</sup> The mathematical background of the procedure was described elsewhere.<sup>[14]</sup>

### Quantum chemical calculations

*Ab initio* HF/6-31G\*\* calculations were done by the Gaussian 98 program suite.<sup>[15]</sup> This level of theory presents an acceptable compromise between the computing costs and accordance with the experimental results.<sup>[16,17]</sup> The well-known weakness of the HF method is the neglect of electron correlation, but it is also quite common that basis set incompleteness introduces errors opposite to that, leading in cases to fortuitously good HF results with medium basis sets.<sup>[18]</sup> At the same time, the use of the DFT calculations for description of the breakage of the IHB in 1-hydroxy-2-naphthol and 2-hydroxy-3-naphthol yields very similar results for the energetics of conversion from closed **E** to open **E'** form.<sup>[19]</sup>

It is worth to mention that the accurate description of the solvent effects remains a major challenge in the quantum chemistry. In this case of study the bulk solvent effects have been estimated by single-point calculations using the polarized continuum model (PCM) with its inborn limitations.<sup>[20,21]</sup> For better description of the specific solvent action in the case of tautomeric processes a mixed approach (continuum solvation model together with addition of the solvent molecules around the solute)<sup>[16,17,22]</sup> has been applied. As one alternative, the inclusion of thermal fluctuations and proper treatment of the solvent mixture would be straightforward by Car–Parrinello simulations, see Reference.<sup>[23]</sup>

Among the common spectral solvents there are several candidates<sup>[9]</sup> with negligible proton donor and substantial proton acceptor abilities for study of the pure proton acceptor effect on the strength of IHB–acetone, ethylacetate, *N,N*-dimethyl formamide, diethyl ether, and DMSO. Acetone has been selected for the current study, because of the lower computational costs.

The change of the relative energy of the enol form as function of the tautomeric proton position has been the main object of interest in the quantum chemical calculations. A gradual change between two border structures, namely closed **E** and open **E'** was considered, corresponding to dihedral angle  $\rho$  (Scheme 1) of  $0^\circ$  and  $180^\circ$ .

The calculations have been performed on four levels:

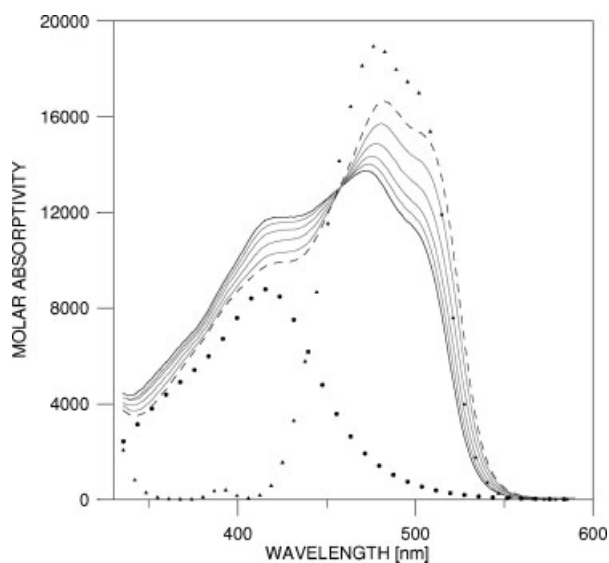
- optimization of both tautomeric forms (**E** and **K**) of **2** and **3** without any restrictions. The resulting structures are planar for **2** and with twisting of the phenyl ring in the case of **3** as expected.<sup>[8,16,17]</sup> Then the energy of conversion of **E** into **E'** was studied as a function of  $\rho$  keeping the rest of the molecule fixed. No molecule acetone was added at this stage.
- optimization of enol–acetone complexes keeping the acetone molecule and the tautomeric molecule fixed. In this case only the intermolecular geometry was optimized as a function of  $\rho$ .
- unrestricted optimization of the enol form–acetone interaction as a function of  $\rho$ .
- unrestricted optimization of the enol form–acetone interaction as a function of  $\rho$  in PCM acetone environment.

In the first three levels of calculation the PCM model was used to describe the solvent effect *as medium* on the already optimized complexes, while true PCM optimization has been performed at the fourth level. Although latter seems more authentic in respect of the real situation in solution it should be noted that not in all cases a convergence has been obtained and the computing costs cannot be fully justified. For this reason only part of the computational results can be discussed.

## RESULTS AND DISCUSSION

### Spectral investigations

The measured spectra of **2** in acetone/chloroform are given on Fig. 1 as an example. As seen the change of the solvent



**Figure 1.** Absorption spectra of **2** in acetone/chloroform binary solvent mixture: 100% acetone (—), 100% chloroform (-----), the volume percentage in the rest of the solutions changes stepwise with 20%. Individual absorption spectra of **2K** (triangles) and **2E** (circles) scaled with a factor of 0.5

composition leads to shift of the tautomeric equilibrium increasing the content of the keto form from acetone to chloroform. The spectral data were processed by using of the previously developed procedure for quantitative analysis of tautomeric mixtures.<sup>[14]</sup> As result the individual spectra of **2E** and **2K** have been estimated along with the tautomeric constants  $K_T$  in each individual solvent.

The corresponding values for acetone and chloroform are 0.377 and 1.24. The value for chloroform is reasonably near to the previously reported<sup>[5]</sup> and there was no previous quantitative data for acetone. Using the same procedure the values of  $K_T$  in DMSO and diethyl ether has been estimated. Although a value for methanol has been published by us before<sup>[5]</sup> the procedure has been performed again using another binary solvent mixture (methanol/water) since the previously used mixture methanol/formamide leads to very high content of the keto form in comparison with the value in ethanol. In addition the value in formamide is an outlier in LSER analysis<sup>[9]</sup>. In order to have real comparability with the current data in the discussion below we have repeated all experiments noted in Reference.<sup>[5]</sup> It has been found that the values of  $K_T$  in all solvents except methanol and formamide are essentially the same as published. In the case of methanol/formamide mixture a substantial differences in the spectra have been found due probably to impurity in the formamide used before. The processing of the current data for methanol/formamide and methanol/water mixtures leads to values of the tautomeric constant 0.77 and 0.83 in methanol which are in a reasonable agreement. The newly estimated value for formamide lies in the range of 1.0–1.5 due to statistical reasons and cannot be used in the following discussion.

The data for the tautomeric constants of **2** determined in the current study and these of **3** taken from the literature are collected in Table 1.

It is worth to be mentioned that in many cases there are substantial differences between the tautomeric constants determined by UV–Vis and NMR spectroscopy<sup>[3]</sup> including compounds under this study. In comparison with UV–Vis spectroscopy, much more concentrated solutions are usually used in NMR for keto/enol equilibrium description and the existence of some sorts of aggregates cannot be excluded. This might be probably the main reason of different values of keto/

**Table 1.** Solvatochromic parameters of the solvents<sup>[29,30]</sup> and corresponding tautomeric constants of **2** and **3**

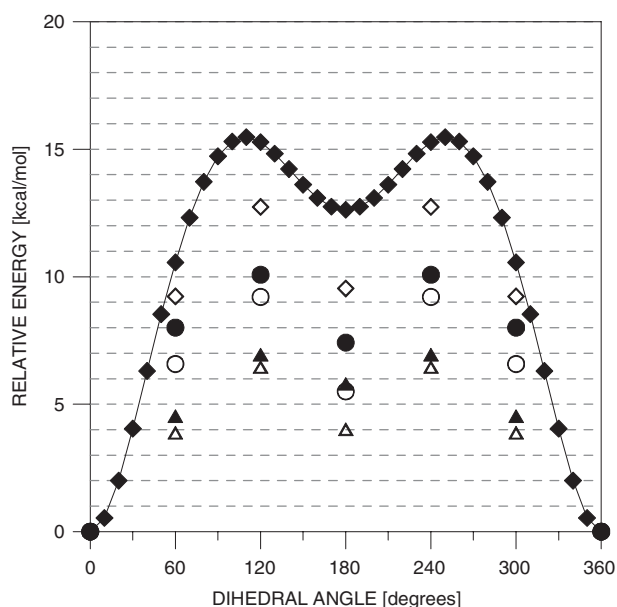
Solvent	log $K_T$				
	$\pi^*$	$\alpha$	$\beta$	<b>2</b>	<b>3</b> <sup>[7]</sup>
Methanol	0.60	0.93	0.62	−0.08	−0.02
Ethanol	0.54	0.83	0.77	−0.21	−0.03
Diethyl ether	0.27	0	0.47	−0.46	−0.87
Acetone	0.71	0.08	0.48	−0.42	−0.48
Acetonitrile	0.75	0.19	0.31	−0.18	−0.25
DMSO	1.00	0	0.76	0.00	−0.12
Methylene chloride	0.82	0.30	0	−0.08	−0.23
Chloroform	0.58	0.44	0	0.09	−0.28
Tetrachloromethane	0.28	0	0	−0.25	−0.83
Hexane	−0.08	0	0	−0.30	−1.06

enol equilibria determined by these two experimental techniques. NMR analysis consists in the fact that the proton exchange between nitrogen and oxygen atoms in the tautomeric azonaphthols and related Schiff bases is fast on the NMR time scale and, thus, only one set of signals is always observed in NMR spectra (NMR data of both individual tautomers are not known). NMR characteristics of model compounds existing either completely in keto or completely in enol forms are utilized, which emphasize the importance of selection of proper model tautomers.

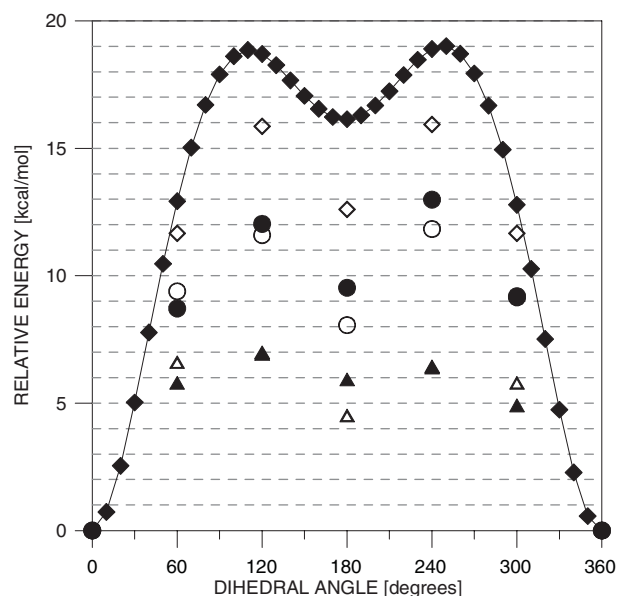
### Quantum chemical calculations in gas phase

The results obtained for optimization of the acetone–enol complexes as a function of the dihedral angle (levels 1–3 as noted in the Experimental Part) in gas phase using PCM solvent environment description of the finally optimized structures are summarized on Figs. 2–4. In contrast to **2** in the case of **3** there are two possible sites for acetone–enol interaction, which have been taken into consideration—with the tautomeric H (OH interaction, Fig. 3, circles) and with the azomethyne H (CH interaction, Fig. 4, circles). The solvation energies of interaction between the enol tautomer and the acetone are summarized on Scheme 2 and give impression for the relative starting points ( $\rho = 0$ ) of Figs. 2–4.

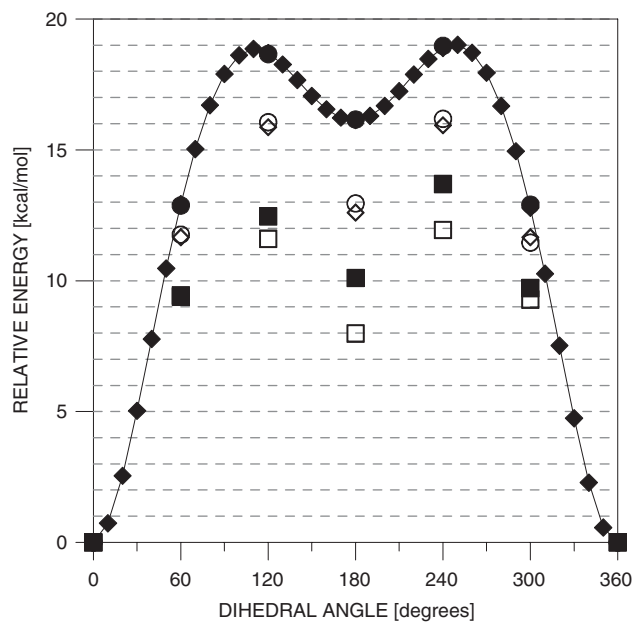
The results for the isolated close (**E**) and open (**E'**) forms (comparing Figs. 2 and 3, rhombs) show that in both cases (gas phase and acetone PCM solvent environment) the energy gap **E–E'** in **3** is with approximately 3.5 kcal/mol higher than in **2**. If we assume this difference as a measure of the IHB strength this fact seems to give a rough answer that the IHB in **2** is weaker. However, the addition of the acetone molecule to interact with



**Figure 2.** Conversion of **2E** into **2E'**—relative energy as a function of  $\rho$ : changing the dihedral angle and keeping the rest of the molecule fixed (rhombs); the enol tautomer with added molecule acetone (OH interaction), optimizing only the intermolecular geometry only (circles); the tautomer with added molecule acetone (OH interaction), keeping only the dihedral angle fixed (triangles). The filled characters are for gas phase and the empty characters are for PCM acetone environment of the optimized structures



**Figure 3.** Conversion of **3E** into **3E'**—relative energy as a function of  $\rho$ : changing the dihedral angle and keeping the rest of the molecule fixed (rhombs); the enol tautomer with added molecule acetone (OH interaction), optimizing only the intermolecular geometry only (circles); the tautomer with added molecule acetone (OH interaction), keeping only the dihedral angle fixed (triangles). The filled characters are for gas phase and the empty characters are for PCM acetone environment of the optimized structures

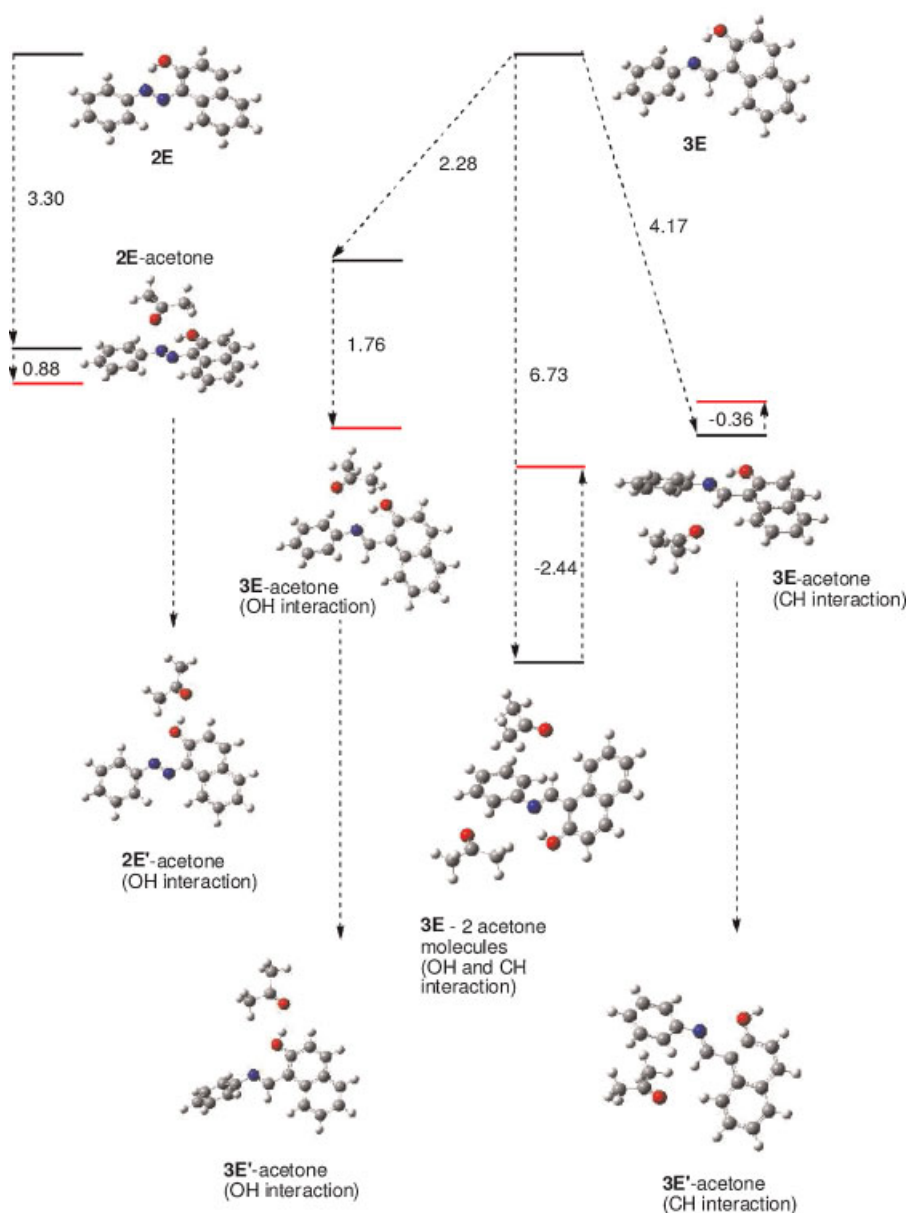


**Figure 4.** Conversion of **3E** into **3E'**—relative energy as a function of  $\rho$ : changing the dihedral angle and keeping the rest of the molecule fixed (rhombs, the same as in Fig. 3, given for clarity); the enol tautomer with added molecule acetone (CH interaction), optimizing only the intermolecular geometry only (circles); the tautomer with added 2 molecules acetone (OH and CH interactions together), optimizing only the intermolecular geometry (squares). The filled characters are for gas phase and the empty characters are for PCM acetone environment of the optimized structures

the tautomeric hydrogen leads to decrease of the value from 2.5 kcal/mol in the restricted optimization case (circles) and finally to 0.5 kcal/mol in the unrestricted one (triangles). A value of 0.5 kcal/mol lies in margin of error and cannot leave to an explicit conclusion. As seen from the pictures of **2E** and **3E** given in Scheme 2, in the closed forms the interactions between tautomeric H (OH interactions) in both compounds and the acetone are not specific, and look like more to long distance dipole solute–solvent interactions. In the case of **3** an additional interaction with the hydrogen from the azomethyne group is possible (CH interaction). Although according to Fig. 4 (circles) this interaction does not affect the relative energy as function of  $\rho$ , the initial closed form complex is preferred by 1.9 kcal/mol in gas phase (Scheme 2). In acetone PCM field both OH and CH interactions seems almost equally possible. Most probably the **3E** form interacts simultaneously with two molecules of acetone

which leads to a substantial stabilization even in gas phase (6.7 kcal/mol). Therefore, in Fig. 4 the complex with two acetone molecules (squares) should be considered as most probable which leads to a energy difference between **3E** and **3E'** of 10 kcal/mol in gas phase—with 2.5 kcal/mol more than the corresponding value in the case of **2** (Fig. 2, circles). Such a difference seems suitable to conclude that the strength of IHB in **2** and **3** is different. Obviously in the case of **3** there is strongly stabilized closed **3E** form, which makes the rotation of the tautomeric hydrogen impossible. In this enol—two molecules acetone complex only specific CH interaction is available and the other acetone molecule, as mentioned above, does not interact with the tautomeric H as proton acceptor.

Additional proof can be found in Table 2, where the relative tautomeric energies ( $\Delta E_{K-E}$ ) are compared with the experimentally obtained tautomeric constants. A positive value of  $\Delta E_{K-E}$



**Scheme 2.** Solvation energies [kcal/mol], calculated as described in ref.,<sup>[17]</sup> of **2E** (left) and **3E** (right) interacting with acetone. The energy levels in acetone environment (PCM) are given in red. The corresponding complexes of **2E'** and **3E'** are shown for clearness

**Table 2.** Relative energies (in kcal/mol) of the tautomeric forms

Compound	$\Delta E_{K-E}$			
	Single tautomer gas phase	Single tautomer in acetone (PCM)	With added molecule acetone in gas phase	With added molecule acetone in acetone (PCM)
<b>2</b>	0.28 (0.49 <sup>a</sup> , 0.56 <sup>b</sup> )	-0.17	-0.90	-0.24 (0.38 <sup>c</sup> )
<b>3</b>	1.76 (0.09 <sup>a</sup> )	0.41 (0.33 <sup>c</sup> )	-1.38 <sup>d</sup> 1.63 <sup>e</sup> -1.57 <sup>f</sup>	-0.31 <sup>d</sup> 0.12 <sup>e</sup> -0.69 <sup>f</sup>

Experimentally determined  $K_T$  in:  
<sup>a</sup> cyclohexane.  
<sup>b</sup> Tetrachloromethane.  
<sup>c</sup> Acetone.  
<sup>d</sup> OH interaction.  
<sup>e</sup> CH interaction.  
<sup>f</sup> Added two molecules acetone: both OH and CH interactions.

supposes more stable **E**-form. There is acceptable agreement the gas phase relative energies and the tautomeric constants in nonpolar solvents which are lower than 1. In the case of **2** the tautomeric constants are higher than in **3**, which corresponds to lower, but still positive relative tautomeric energy. In acetone in the case of **3** the CH and OH interactions lead to opposite effects, canceling each other and the simple acetone field with  $\Delta E_{K-E} = 0.41$  kcal/mol is in reasonable agreement with the increased content of the keto form, still dominated by the enol tautomer. The value of the tautomeric constant of **2** in acetone, being less than 1, needs a special discussion. Such value contradicts on the  $\Delta E_{K-E}$  values in acetone (last three columns), which are negative and suppose more stable **K**-form. Quite surprisingly this tautomeric constant is lower even comparing with these in less polar solvents like cyclohexane and tetrachloromethane. It is especially clear from Fig. 1, where increase in the content of the less polar solvent (chloroform) in the binary mixture leads to shift of the equilibrium to the more polar keto tautomer. An additional stabilization of the enol form through breakage of the IHB could be a possible explanation for the situation in acetone.

### Structure optimization of the enol–acetone complexes in PCM field

Due convergence problems in acetone PCM field it has been impossible to perform in full scale the optimization variants described above. In the case of **2** the optimization leads to further decrease of the **E–E'** gap (2.6 kcal/mol) in comparison with the data shown in Fig. 2 (open triangles), which support the general hypothesis for weaker IHB.

Concerning **3** only the individual OH and CH interactions modeling was successful yielding results for the **E–E'** gap 4.3 and 10.5 kcal/mol, respectively. The optimization of the interaction enol—two acetone molecules (OH and CH interaction together) failed, which do not allow an explicit conclusion.

Comparing the above mentioned gaps with these in Figs. 2–4 tend for decreasing is evident as result of the optimization in PCM field. At the same time the overall picture is essentially the same as in gas phase. Therefore, it should be assumed that the gas

phase optimizations (levels 1–3) give a reasonable approximation of the real situation in solution.

### LSER analysis

According to the LSER theory<sup>[29,30]</sup> the tautomeric constant can be presented in a quantitative manner according to Eqn (2) through three solvent parameters.

Some of the data collected in Table 1 have been analyzed already<sup>[9]</sup> and the corresponding linear equation for **3** can be taken without change (The standard deviations are given in the brackets.)

$$\log K_T = -1.05(0.04) + 0.85(0.07)\pi^* + 0.60(0.06)\alpha, \quad r^2 = 0.976 \quad (3)$$

The proton acceptor term tends to zero, which excludes proton acceptor interactions.<sup>[9]</sup>

In the case of **2** a new equation has been derived including the newly obtained values:

$$\log K_T = -0.27(0.04) + 0.13(0.07)\pi^* + 0.48(0.07)\alpha - 0.52(0.08) \cdot \beta, \quad r^2 = 0.937 \quad (4)$$

The value in DMSO remains an outlier in the fitting procedure probably because it behaves in this case as polar medium rather than strong proton acceptor solvent.<sup>[24–28]</sup> The correlation coefficient of Eqn (4) and the deviation in the fitted terms are improved,<sup>[9]</sup> but the introduction of the new values does not affect the fitting terms essentially. Here the proton acceptor term remains substantial and negative, which means that the enol form is favored by such solvents. According to the quantum chemical calculations discussed above the only specific interaction in this molecule is possible through breakage of the IHB to the open **2E'** form.

If we assume that **E** and **E'** coexist the following overall equilibrium scheme could be written down:



with equilibrium constants  $K_T$  (Eqn (1)) and  $K_e$  (a measure for the IHB breakage):

$$K_e = \frac{[E']}{[E]} \quad (5)$$

From the structures of **2E** and **2E'** we can assume little UV-Vis spectra difference (otherwise no isosbestic point could be observed in Fig. 1), which means that the experimentally determined tautomeric constant in this case can be presented as:

$$K_{T_{\text{obs}}} = \frac{[K]}{[E] + [E']} \quad (6)$$

and hence

$$K_{T_{\text{obs}}} = \frac{K_T}{1 + K_e} \quad (7)$$

According to Eqn (7) if a breakage of the IHB occurs and there are substantial amount of the open **E'** form, the experimentally determined tautomeric constant should be lower than the real one. Actually this is observed in the case of **2**.

Such hypothesis can be easily confirmed or rejected by the LSER analysis. If we take into account the solvents without proton acceptor abilities (last four in Table 1) and fit only them, the predicted value of  $K_T$  in acetone could be the same as if it does not interact as proton acceptor (i.e., it reflects the equilibrium as medium through the dielectric constant value). Such fit for **2** yields Eqn (8):

$$\log K_T = -0.27(0.04) - 0.03(0.13)\pi^* + 0.84(0.23)\alpha, \quad r^2 = 0.968 \quad (8)$$

Using the solvatochromic parameters from Table 1, one can calculate a value of 0.6 for  $K_T$  in acetone. Such value is reasonable taking into account the corresponding tautomeric constants in other solvents with similar polarity.<sup>[5]</sup> Returning to Eqn (7) it gives a value of 0.59 for  $K_e$ , which means that in acetone coexist 27% **2E'**, 46% **2E**, and 27% **2K**. Of course these values are only approximation taking into account the unavoidable statistical deviation in Eqn (8), which give approximate limits for the above predicted  $K_T$  from 0.46 to 0.76. However, even without exact values the discussion yields a clear conclusion that in proton acceptor solvent, like acetone, two different enol form coexist, namely: **2E** stabilized by the action of acetone as medium (nonchelated) and **2E'**, where the IHB is broken and the specific proton acceptor abilities of the solvent play stabilization role (chelated).

Using the concept described by Eqns (5–8) an analysis of the effect of proton acceptor properties of the solvents listed in Table 1 on the IHB of **2** can be performed. As expected (Fig. 5) there is a trend between the proton acceptor abilities of the solvents ( $\beta$  value) and the amount of the open enol form (estimated values of  $K_e$ ).

If the same LSER hypothesis is applied to **3**, the corresponding equation is:

$$\log K_T = -1.01(0.04) + 0.65(0.01)\pi^* + 0.80(0.02)\alpha, \quad r^2 = 0.999 \quad (9)$$

and the predicted tautomeric constant is 0.33, which is exactly the same as determined.<sup>[7]</sup> The value of  $K_e$  tends to zero.

Hence, we can finally conclude that the IHB in **2** is weaker than that in **3**. As result it is partially broken by proton acceptor solvents, which explains in a reasonable way the previously

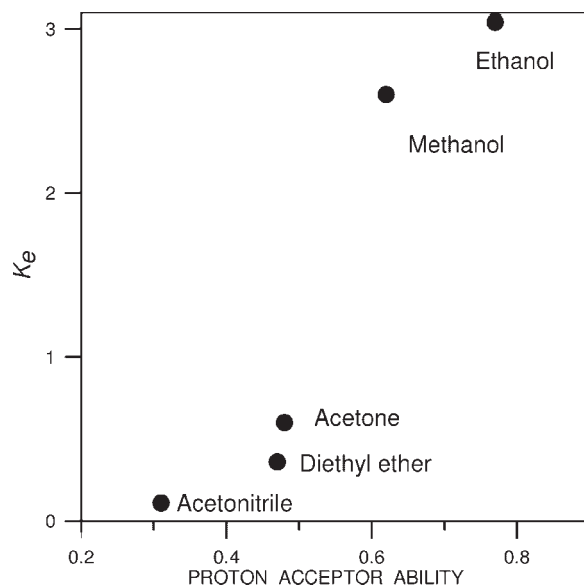


Figure 5.  $K_e$  values versus  $\beta$  values

observed, and described in the Introduction Part, experimental facts.

## Acknowledgements

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