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Tautomerism of 2-hydroxynaphthaldehyde Schiff bases†

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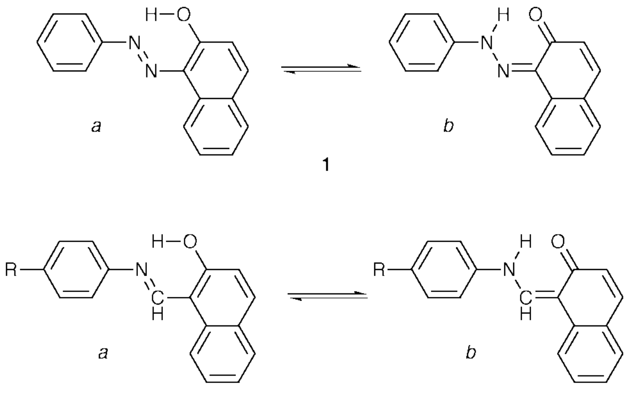
A UV–Vis spectroscopic study based on the recently developed chemometric approach for quantitative analysis of undefined mixtures is performed on a series of donor and acceptor substituted Schiff bases of 2-hydroxynaphthaldehydes. In CCl_4 solution all compounds preferentially exist as the phenol tautomer independent of the nature of the respective substituent. With increasing polarity the tautomeric equilibrium is shifted towards the quinone form. In $CHCl_3$ and, especially, ethanol a clear distinction between the effect of donors (stabilization of the quinone form) and acceptors (stabilization of the phenol tautomer) is evident. *Ab initio* calculations including solvent effects *via* the polarized continuum model of solvation as well as the supermolecule approach are used to rationalize the experimental findings.

Introduction

The nature of tautomeric processes has attracted considerable attention, both from experimental and theoretical points of view. Of particular interest are the causes of proton exchange among strong hydrogen bonds, like those in 1-phenylazo-2-naphthols and *N*-(2-hydroxy-1-naphthylmethylidene)anilines (Scheme 1). It has been shown experimentally[1] and confirmed theoretically[2] that the compound **1** contains significant amounts of both *a* and *b* forms in the gas phase as well as in solution, depending on the nature of the solvent used. Furthermore a significant shift in the tautomeric equilibrium has been detected in both phases upon changing the substituent R.[3,4] Since intramolecularly hydrogen bonded Schiff bases, *e.g.* **2**–**10**, have attracted considerable attention because they exhibit thermochromism and photochromism,[5] the study of their structure related properties, like tautomerism, is of special importance. As might be anticipated on a rather intuitive basis, these Schiff bases could also have appreciable amounts of phenolic tautomer *a* in equilibrium with the quinoid tautomer *b*.



2 R = H
4 R = CH_3
6 R = Cl
8 R = I
3 R = $N(CH_3)_2$
5 R = OCH_3
7 R = Br
9 R = CN
10 R = NO_2

Scheme 1

However, due to the high proton exchange rate it is not possible to isolate the individual tautomeric forms. Consequently, quantitative analyses of these processes, as well as relationships between structural properties and tautomers, are difficult to obtain. Although there are some studies based on NMR approximations[6] which shed light on different aspects of this kind of tautomerism, up to now an in depth study concerning the tautomeric properties of 2-hydroxynaphthaldehyde Schiff bases with special emphasis on the effects on the substituents and the solvents was not available.

In the present work we report a UV–Vis spectroscopic study of the tautomeric equilibrium of **2**–**10** in different solvents and at different temperatures. This study is possible due to the recently developed chemometric approach for quantitative analysis of undefined mixtures based on resolution of overlapping bands.[7] The reliability of this method has already been demonstrated for the determination of tautomerization constants of tautomeric azo dyes **1** and their analogues.[1,8] The changes of the equilibrium compositions with the nature of R and the kind of the solvent are detected and attempts to explain these results on a theoretical basis have been made by use of quantum chemical calculations.

Experimental

All compounds studied were prepared by standard procedures.

The sets of spectra of isomolar solutions of each compound in mixed solvents with different solvent compositions were recorded on a PE Lambda 5 UV–Vis spectrophotometer using spectral grade solvents. These sets of spectra were then analyzed by a quantitative procedure based on a three-step resolution of overlapping bands. Thereby an estimation of both tautomerization constants and individual spectra of the

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† *Ab initio* (HF/6-31G** and HF/6-311G**) gas phase total energies are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b000798f

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Table 1 Tautomeric constants of **2** and individual spectral characteristics of both tautomeric forms in different solvents

Solvent	Relative permittivity	K_T	λ_{max} *a*-form/nm	λ_{max} *b*-form/nm
Water	80.4	3.35[c]	348[a]	(455,437,409s)[a] (465,438,411)[b]
Dimethyl sulfoxide	46.7	0.751	380[a]	(458,439)[a]
Acetonitrile	36.0	0.562	375[a]	(452,432)[a] (458,430,405)[b]
Methanol	32.6	0.950	355[a] (386,358)[b]	(454,436,408s)[a] (462,434,410)[b]
Ethanol	24.3	1.110	376[a]	(458,438)[a] (462,441,411)[b]
Acetone	21.4	0.333	376[a]	(454,434)[a] (464,435,410)[b]
Dichloromethane	8.9	0.587	375[a]	(455,436)[a] (464,437,410)[b]
Chloroform	4.8	0.522	376[a]	(456,440)[a] (467,438,413)[b]
Diethyl ether	4.3	0.136	375[a]	(452,432s)[a] (461,433,404)[b]
Carbon tetrachloride	2.24	0.149	377[a]	(457s,436s)[a] (468,440,411)[b]
Hexane	1.88	0.087	375[a]	(457s,432s)[a] (461,433,405)[b]

[a] Observed maxima. [b] Determined by fourth derivative spectroscopy.[9] [c] Approximation on the basis of ethanol–water mixture.

tautomers is performed. The individual steps in this approach include:

first step—initial approximations of the number of overlapping bands and their positions by second and fourth derivative spectroscopy;[9]

second step—initial approximations for the bands' intensities and widths and their assignment to the respective tautomeric forms according to;[10]

third step—final refinement by simultaneous resolution of the whole set of spectra.[7]

The thermodynamic measurements were performed in ethanol using the thermostatic equipment Julabo 6A with a precision of ±1 °C. The set of spectra recorded at different temperatures was processed as described above.

All spectra were always recorded within the first 10 minutes following the preparation of the solution since the hydrolysis of Schiff bases may take place in solvents containing water. The measurements of compounds **9** and **10** in ethanol were the only exception due to their poor solubility. However, in the calculations the above mentioned hydrolysis was taken into account, performing the calculation procedure in the multicomponent mixture version,[7] causing at the same time lower precision of the tautomeric constants.

All semiempirical calculations were done by the AM1[11] as well as the PM3[12] Hamiltonian using the VAMP program package.[13] Geometries were completely optimized by the eigenvector following routine[14] without any restrictions. At the semiempirical level solvent effects were treated by the SCRF approximations[15] using a van der Waals shaped cavity and scaling factors of 1.6 ($CHCl_3$) and 1.2 (H_2O) for van der Waals radii.[16] *Ab initio* (HF/6-31G** and HF/6-311G** basis sets) calculations were done by the GAUSSIAN94 program suite.[17] Solvent effects were treated by the polarized continuum model (PCM).[18,19] Electronic excitation energies were calculated by the semiempirical ZINDO program[20,21] including solvent effects according to Zerner.[22]

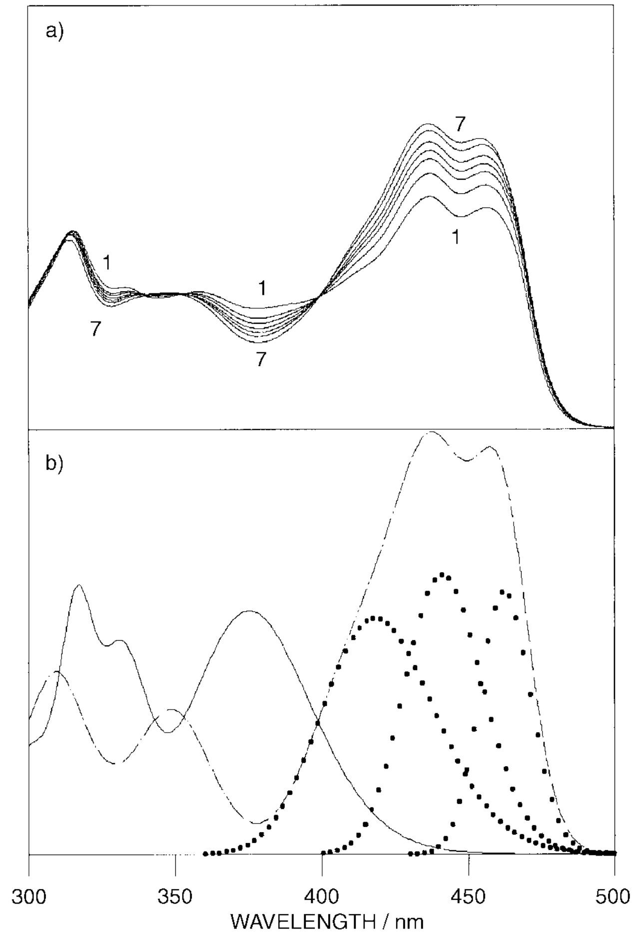

Fig. 1 (a) Spectra of **2** in EtOH–water, solvent composition (spectra 1, 100% EtOH; spectra 7, 40% EtOH); (b) calculated individual spectra of both tautomeric forms (——— *a* form; ---- *b* form). The individual sub-bands composing the long wavelength band of *b* are given in dots.

Results and discussion

The absorption spectra of **2** in ethanol–water solvent mixtures varying the solvent composition are presented in Fig. 1. The observed spectral changes are interpreted in terms of an $a \rightleftharpoons b$ equilibrium.[23] It is evident that increasing the water content leads to an increase of the amount of the *b* form (corresponding to the complex band at ~430 nm) in the solvent mixture, whereas the opposite is true for the *a* form (the bands at ~370 nm). The spectra in ethanol–water and in other binary solvent mixtures were processed as described above and the results for the tautomerization constants K_T (defined as the [*b*]/[*a*] ratio) along with the calculated spectral characteristics of the pure tautomeric forms are collected in Table 1. It is evident that—although there is a trend towards an increase of K_T with increasing solvent relative permittivity—the solvent effect cannot in general be correlated with the solvent polarity due to possible specific solute–solvent interactions. The individual spectra of both tautomeric forms do not show evidence of solvatochromism. As seen in Table 1 for **2** one observes band maxima at 375–376 nm for the *a*-form and at 457–458 nm for the *b*-form in both ethanol and CCl_4. Furthermore, the calculated molar absorptivities of the major *a* and *b* bands as well as the oscillator strengths in all solvents used are practically the same.

Thermochemical parameters ($\Delta H°$/kcal mol^{-1} and $\Delta S°$/cal mol^{-1} K^{-1}) for compounds **2**–**8** are summarized in Table 2. Clearly, the equilibrium $a \rightleftharpoons b$ shifts towards the phenol tautomer *a* with increasing temperature. From the thermodynamic point of view the process is exothermic ($\Delta H° = -1.2$ to -2.1 kcal mol^{-1}) with the $-T\Delta S°$ term being of nearly the same size but opposite sign ($\Delta S° = -4.8$ to -6.2 cal mol^{-1} K^{-1}). It can be seen that for acceptor substituted derivatives (R = Cl, Br, I) $\Delta H°$ is slightly less negative than for the derivatives with R = H and OCH_3. Because of strongly overlapping bands the results for compound **3** are less reliable.

It should be pointed out that these values determined by the UV–Vis method outlined above are in excellent agreement with those reported on the basis of NMR investigations.[3] To study the effect of the substituent R in **2**–**10** as well as the solvent on K_T, the whole set of compounds was measured in EtOH and in $CHCl_3$ as well as in some other solvents. The results are given in Table 3 along with pertinent literature data. Also listed are the Hammett's constants of the substituents. Analyzing the results two interesting but conflicting conclusions can be drawn. On the one hand there is a clear distinction in EtOH and $CHCl_3$ solutions between donor *vs.* acceptor substituents with respect to their effect on the tautomerization constants K_T. The phenolic form *a* is preferentially stabilized by acceptor substituents, while donors shift the equilibrium towards the quinoid form *b*. However, especially in $CHCl_3$ solutions, the effects are quite small and there is little quantitative correlation between K_T and Hammett's σ constants. Such a conclusion is rather surprising, since the substituent effect on the tautomeric properties of the structurally related azo compound **1** and its analogues[1,2,4,8] is clearly opposite. Unfortunately, most of the literature data are based on a variety of assumptions and are therefore unsuitable for comparison purposes. The only exception are the results of Nagy *et al.*[24] published recently which in general support our data. On the other hand, in apolar solvents (*e.g.* CCl_4, see Table 3) the tautomerization constants are essentially independent of the nature of the substituent R. Thus, the substituent effects observed in EtOH and—to a lesser extent—$CHCl_3$ will not be a simple function of the donor–acceptor properties of R.

To shed some further light on this peculiar behavior quantum chemical calculations (semiempirical and *ab initio*) on these molecules were performed. Relevant results (gas and solution phase tautomerization energies) are collected in Table 4. The semiempirical AM1 method—independently of the physical state (gas phase or solution) as well as the respective substituent—invariably predicts greater stability of the quinone tautomer *b*. In contrast, using the PM3 Hamiltonian, without exception a clear preference for the phenol form *a* is calculated. In view of these results the excellent agreement between the experimental tautomerization enthalpy for compound **2** in EtOH ($\Delta H° = -1.8$ kcal mol^{-1}) with that obtained by AM1 ($\Delta H° = -1.7$ kcal mol^{-1}, see Table 4) must be considered as fortuitous. According to the *ab initio* results, in the gas phase there should be a clear preference for the phenol tautomer *a*. Inclusion of bulk solvent effects *via* the polarized continuum model (PCM) of solvation[18,19] leads to a shift of the tautomeric equilibrium towards the quinone *b*. In $CHCl_3$ as the solvent there should still be a slight predominance of the phenol tautomer, whereas in EtOH—except for the acceptor substituted derivatives **6** (R = Cl) and **9** (R = CN)—the quinone tautomer *b* is calculated to be slightly more stable. Both basis sets used (6-31G** and 6-311G**) yield essentially identical results. Finally, both types of substituents (donors as well as acceptors) lead to a bathochromic shift of the UV–Vis spectra of both tautomers.

Table 2 Thermodynamic parameters of the equilibrium $a \rightleftharpoons b$ in ethanol

Substituent	$\Delta H°$/kcal mol^{-1}	$\Delta S°$/cal mol^{-1} K^{-1}
$N(CH_3)_2$	−1.595 ± 0.126	−4.995 ± 0.413
CH_3	−2.061 ± 0.117	−5.951 ± 0.385
OCH_3	−2.089 ± 0.185	−6.153 ± 0.608
H	−1.848 ± 0.130	−6.308 ± 0.426
Cl	−1.225 ± 0.207	−4.800 ± 0.678
Br	−1.298 ± 0.291	−4.616 ± 0.917
I	−1.586 ± 0.198	−5.946 ± 0.652

Table 3 Calculated tautomeric constants compared with the Hammett constants of the substituents

Substituent	σ_n	K_T Ethanol	K_T $CHCl_3$	K_T Various solvents	K_T Lit.[a]
$N(CH_3)_2$	−0.171	1.267	0.667	CCl_4 0.149	1.5[6c]
CH_3	−0.129	1.723	0.555	DMSO 0.727 Methanol 1.110 CCl_4 0.121	1.32[6a] 1.27[24]
OCH_3	−0.111	1.673	0.754	DMSO 1.114 CCl_4 0.118	0.69[6a] 1.27[24] 0.61[6b] 1.3[6c]
H	0.000	1.110	0.522	See Table 1	0.11[6a] 1.07[24] 1.8[9]
Cl	0.238	0.745	0.515	CCl_4 0.109	0.74[24]
Br	0.265	0.805	0.351	DMSO 0.574 Methanol 0.780 CCl_4 0.111	0.66[6a]
I	0.299	0.814	0.492	CCl_4 0.121	
CN	0.674	0.532	0.416	CCl_4 0.146	
NO_2	0.778	0.562	0.413	CCl_4 0.136	0.66[6a] 1.3[6c]

[a] Literature data: in MeOH by NMR approximation;[6a] by UV–Vis spectroscopy in EtOH after addition of $CaCl_2$;[24] in MeOH by PCA;[6b] in $CDCl_3$ by ^{13}C NMR.[6c]

Table 4 Tautomerization energies (kcal mol^{-1}) of the phenol and quinone tautomers of compounds **2**–**10** obtained by semiempirical AM1 and PM3 and *ab initio* (HF/6-31G** and HF/6-311G**; zero point energy (ZPE) corrections calculated at the HF/6-31G** level of theory are included) calculations (a negative sign indicates greater stability of the quinone tautomer)[a]

	AM1			PM3		
R	Gas	$CHCl_3$[b]	H_2O[b]	Gas	$CHCl_3$[b]	H_2O[b]
$N(CH_3)_2$	−1.3	−1.3	−1.4	3.0	3.0	3.0
CH_3	−1.6	−1.6	−1.7	2.9	2.9	2.8
OCH_3	−1.2	−1.2	−1.2	3.4	3.4	3.4
H	−1.6	−1.6	−1.7	2.9	2.9	2.8
Cl	−1.3	−1.3	−1.3	3.0	3.0	3.0
Br	−1.5	−1.5	−1.5	3.0	3.0	3.0
I	−1.6	−1.6	−1.6	3.0	3.0	3.0
CN	−1.5	−1.5	−1.5	3.0	3.0	3.0
NO_2	−1.5	−1.5	−1.5	2.6	2.6	2.6
	HF/6-31G**			HF/6-311G**		
	Gas	$CHCl_3$[c]	EtOH	Gas	$CHCl_3$[c]	EtOH
$N(CH_3)_2$	1.2	0.7	−0.5	1.4	0.9	−0.4
OCH_3	1.9	1.0	−0.7	2.0	1.0	−0.5
(+1 MeOH)	−2.0		−1.9			
H	1.8	0.7	−0.5	1.9	0.8	−0.2
(+1 MeOH)	−2.0		−2.4			
(+1 $CHCl_3$)	−0.6	−0.9				
Cl	2.3	1.3	0.0	2.4	1.4	0.2
(+1 MeOH)	−1.6		−1.6			
CN	2.2	1.3	0.2	2.4	1.4	−0.4

[a] AM1 and PM3 heats of formation as well as *ab initio* total energies are available from the authors upon request. [b] SCRF model of solvation. [c] PC model of solvation.

Except for halogen derivatives **6**–**8**, the ZINDO[20–22] calculated excitation energies are in agreement with these experimental observations (see Table 5).

Effect of the solvents

Generally, solvent effects on K_T can be separated into specific solute–solvent, *e.g.* hydrogen bonding, and nonspecific bulk interactions. Clearly, only the latter ones are treated by the solvent models used in the quantum chemical calculations. Based on a previous investigation concerning the tautomerism of 1-phenylazo-4-naphthol compounds the solvents used can be divided into several groups depending on their type of interactions with the respective—azo or hydrazo—tautomer:[25]

tautomer-H ··· OH-solvent interaction (*via* moveable proton and the oxygen of the solvent)—EtOH, MeOH and water;

tautomer-O ··· H-solvent interaction (*via* the tautomeric oxygen and the proton/protons from the solvent)—$CHCl_3$ and CH_2Cl_2;

tautomer-H ··· O=solvent interaction (*via* the moveable proton and the double bonded oxygen from the solvent)—acetone and DMSO;

solvents which do not participate in specific interactions.

For the present systems, which are characterized by a strong intramolecular hydrogen bond, one expects a somewhat different behavior towards the solvents used. For instance, the dominating tautomer-H ··· OH-solvent interaction with alcohols in 1-phenylazo-4-naphthols would require breaking of the intramolecular hydrogen bond in compounds of type **2**. Thus, for these molecules a tautomer-O ··· H-solvent interaction with alcohols as well as $CHCl_3$ should be energetically more favorable. Specific interactions of the tautomer-H ··· O=solvent interaction (DMSO, acetone) should hardly be possible because of unfavorable steric repulsions. Besides specific interactions, of course, solvents of the first three groups will also act as a bulk medium. A plot of the relative permittivities of the solvents as a measure of the bulk medium effect *vs.* the tautomerization constants (Table 1) is presented in Fig. 2. It can be seen that the solvents from the first two groups lie out of the correlation, while all other solvents are clearly correlated ($r^2 = 0.988$). The lack of a clear specific effect for DMSO and acetone is in line with the expectations described above. Using the correlation from Fig. 2, a value for the tautomerization constant of **2** at a relative permittivity 0 (or in a vacuum) was estimated to be 0.076 ± 0.001 corresponding to a gas phase ΔG value of *ca.* +1.5 kcal mol^{-1}, to be compared with the corresponding *ab initio* results of +1.3 (HF/6-31G**) and +1.4 kcal mol^{-1} (HF/6-311G**). The deviation from this correlation line (see Fig. 2) might be considered as a measure of the amount or strength of such specific interactions. To further elucidate the effect of solvents, *ab initio* calculations (HF/6-31G**) on

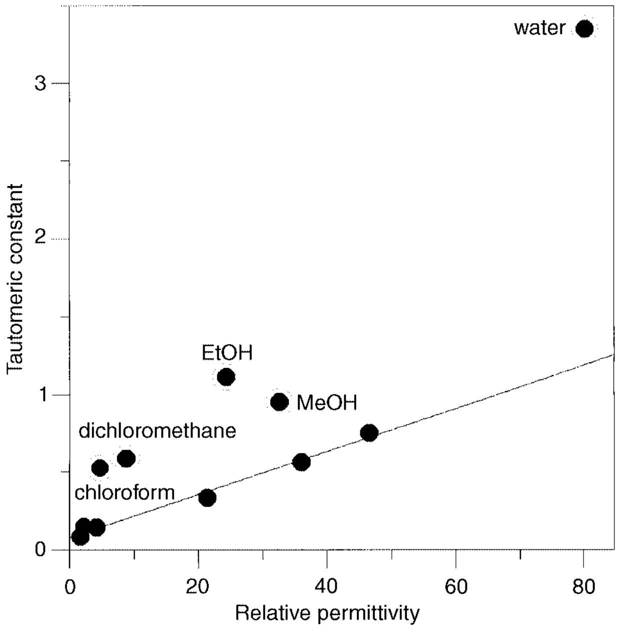

Fig. 2 Relation between the tautomeric constants of **2** and the relative permittivities of the solvents used.

Table 5 Spectral characteristics of the pure tautomeric forms in ethanol estimated from their individual spectra compared with the ZINDO calculated excitation energies and oscillator strengths (based on AM1-SCRF geometries)

	b form						*a* form					
	ZINDO results		Observed maxima		Sub-bands		ZINDO results		Observed maxima		Sub-bands	
R	λ_{max}	f[a]	λ_{max}	ε_{max}	λ_{max}	f[a]	λ_{max}	f[a]	λ_{max}	ε_{max}	λ_{max}	f[a]
H	372	0.50	438	23850	418	0.159	341	0.38	376	13730	376	0.206
			458	22980	441	0.116						
					462	0.065						
						0.340[b]						
CH_3	380	0.54	440	24590	419	0.164	343	0.43	378	18250	378	0.246
			461	23100	446	0.127						
					468	0.062						
						0.353[b]						
OCH_3	388	0.58	445	20140	424	0.141	348	0.56	383	21630	385	0.247
			467	17840	450	0.100						
					471	0.047						
						0.288[b]						
Br	364	0.56	442	23110	423	0.150	345	0.49	378	15610	381	0.234
			461	22610	445	0.109						
					467	0.067						
						0.326[b]						
Cl	365	0.56	441	19220	421	0.116	347	0.51	376	12820	378	0.191
			460	18680	444	0.100						
					466	0.057						
						0.273[b]						
I	367	0.58	444	24220	424	0.159	343	0.47	381	15150	383	0.224
			464	23770	447	0.114						
					469	0.070						
						0.333[b]						
$N(CH_3)_2$	386	0.58	470	37600	448	0.267	350	0.58	412	25960	413	0.331
					482	0.267						
					512	0.049						
						0.583[b]						
CN	378	0.62	448	22440	421	0.080	373	0.67	387	16950	391	0.257
			466	21470	447	0.111						
					471	0.110						
						0.301[b]						
NO_2	399	0.41	456	26370	427	0.111	393	0.64	390	15520	399	0.289
			480s	23440	460	0.062						
					487	0.155						
						0.328[b]						

[a] Oscillator strength. [b] Total value.

the tautomers of **5** (R = OMe), **2** (R = H), and **6** (R = Cl) using the supermolecule approximation, including one molecule of methanol (see Table 4) and, in addition for **2**, calculations with one molecule of $CHCl_3$ were performed. Both methanol and $CHCl_3$ lead to calculated structures indicating—as already mentioned above—hydrogen bonds involving the H-atom of the solvent and the oxygen (hydroxy or oxo) of the solute as characteristic for the second type of solvent (see Fig. 3). In agreement with the results for the $CHCl_3$ complexes, recently $CH\cdots O$ hydrogen bonds involving alkyl halogenides have been shown to behave very much like conventional $OH\cdots O$ H-bonds.[26] Not surprisingly, these interactions appear to be stronger in the case of the quinone tautomer, thus shifting the tautomeric equilibrium towards this form.

Effect of the substituents

In apolar solvents, *e.g.* CCl_4, substituents hardly affect the position of the tautomeric equilibrium $a \rightleftharpoons b$. In striking contrast, in polar solvents, *e.g.* $CHCl_3$ and, especially, EtOH, there is a clear distinction between donor and acceptor substituents. Surprisingly, contrary to the related phenylazonaphthols,[1,2,4,8] in the 2-hydroxynaphthaldehyde Schiff bases **2**–**10** (see Table 3) acceptors shift the equilibrium towards the phenolic form *a*, while donors favor the *b* form. According to the *ab initio* calculations there should be a clear preference for the phenol tautomer *a* in the gas phase, independent of the nature of the substituent. However, in the gas phase acceptor substituted derivatives show a slight energetic shift towards the phenol form (see Table 4). The determination of the thermochemical parameters (see Table 2) indicates that enthalpic and entropic contributions to K_T are of similar magnitude but opposite sign. The exact position of the tautomeric equilibrium, thus, is expected to be governed by a delicate interplay between these two contributions.

From the calculations it also seems evident that especially in solvents where specific interactions are important, this distinction between donor and acceptor substituents is more pronounced. Furthermore, according to the *ab initio* calculations, in acceptor substituted derivatives the phenol tautomers have a higher calculated dipole moment. The contrary is found for the unsubstituted, as well as for 4-donor substituted, derivatives. One therefore expects a shift of the tautomeric equilibrium towards the quinone form *b* for donor substituted derivatives with increasing solvent polarity. The plot of the relative dipole moments of **2**–**10** *vs.* the tautomeric constants is given in Fig. 4. As can be seen there is a trend (where OMe is the only exception), for an increasing difference between the dipole moments of the respective tautomeric forms (*i.e.* *b* being more polar than *a*) leading to an increase of K_T. A possible explanation of this fact could be the twisting around the N–Ph bond frequently found for Schiff bases.[27] However, our calculations (HF/6-31G**) show for the quinone form of **9** an exactly planar structure. But in the case of nonplanarity the substituents cannot really affect the tautomeric fragment. Therefore, relative dipole

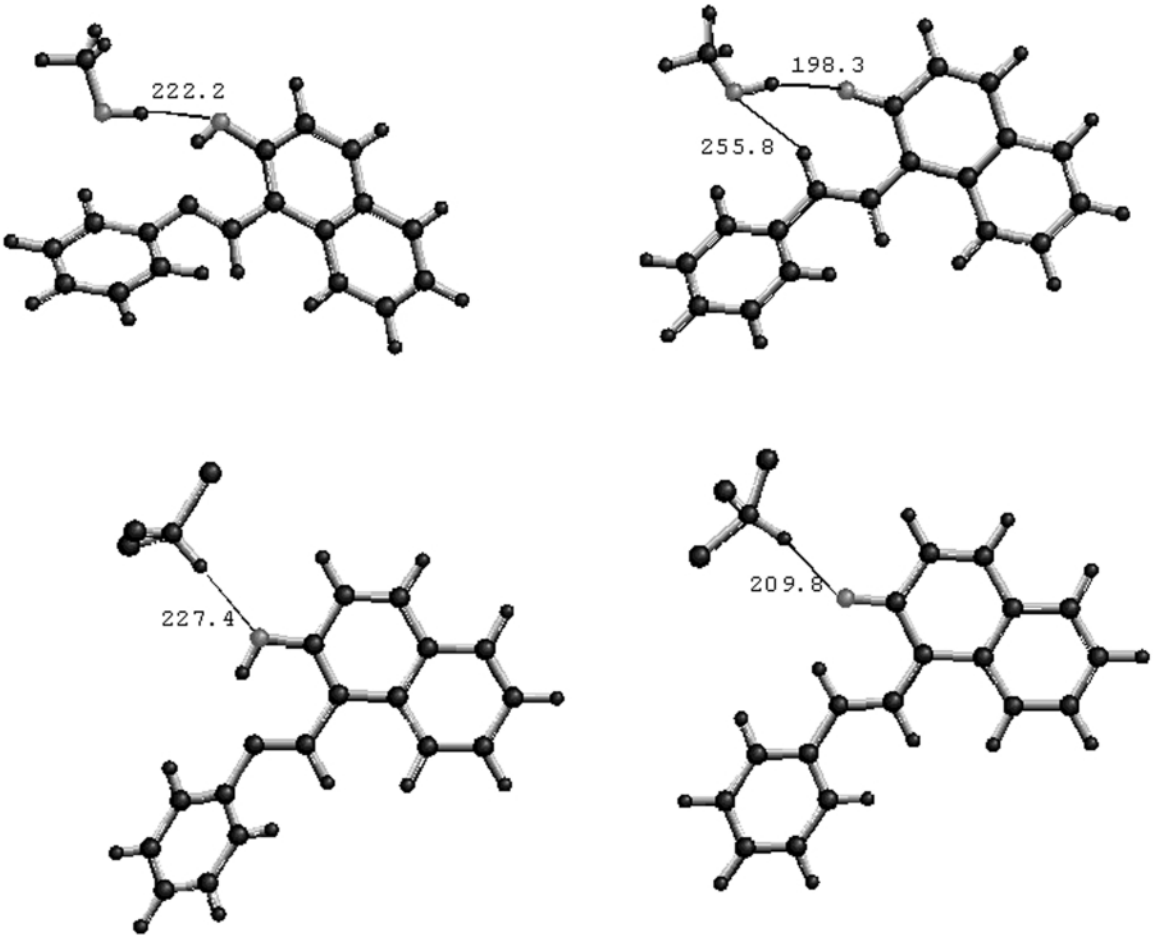

Fig. 3 Calculated (HF/6-31G**) complexes of both tautomers of compound **2** with MeOH and $CHCl_3$ (hydrogen bond distances are given in pm).

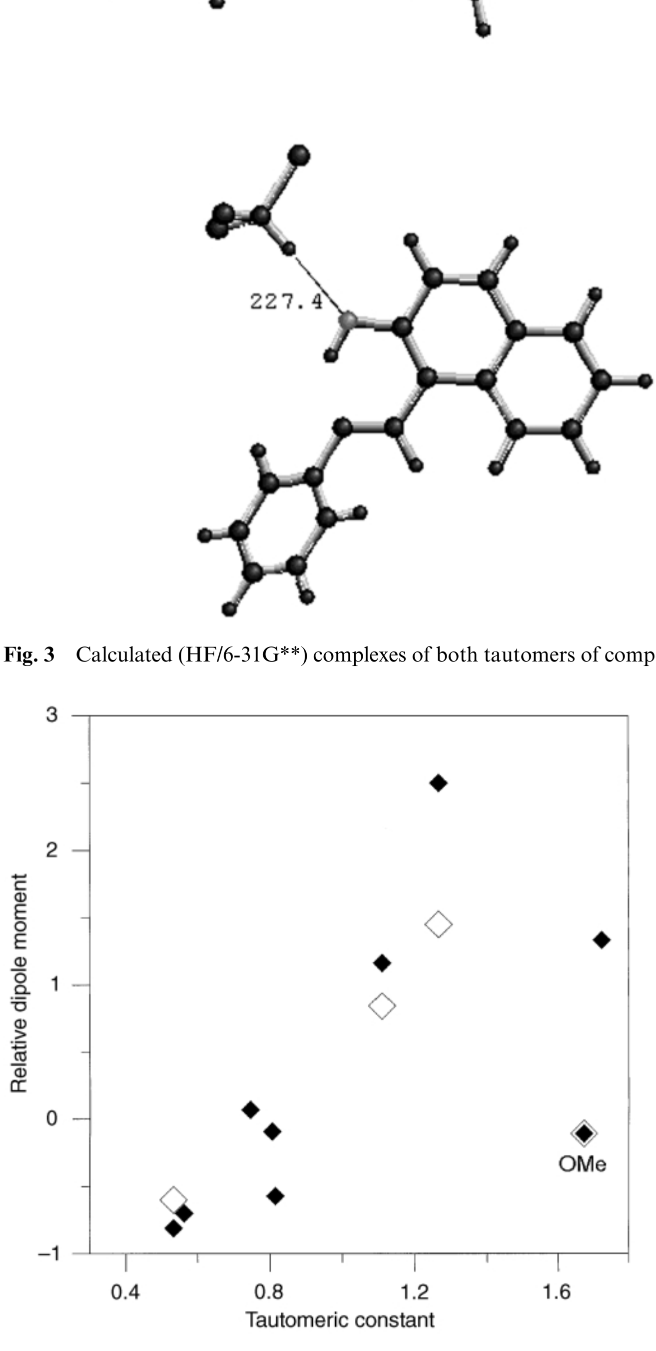

Fig. 4 Relation between the tautomeric constants of **2**–**10** in ethanol and the relative dipole moments of the tautomers (◆ AM1; ◇ HF/6-31G** basis).

moments could play a major role in particular tautomer stabilization.

Conclusion

The following main conclusions can be drawn from the present investigation: (i) Schiff bases of 2-hydroxynaphthaldehyde show phenol–quinone tautomerism with the phenol form *a* dominating in apolar solvents, but the substituents have hardly any effect on the position of this equilibrium. (ii) In polar solvents the equilibrium is shifted towards the quinone form *b*. In EtOH and—to a somewhat lesser extent—$CHCl_3$, donor and acceptor substituents preferentially stabilize the quinone and phenol tautomer, respectively. This substituent effect is in contrast to that found in the related phenylazonaphthols.[1,2,4,8] (iii) In EtOH the equilibrium $a \rightleftharpoons b$ is exothermic with $\Delta H° = -1.2$ (R = Cl) to -2.1 kcal mol^{-1} (R = CH_3O). The entropic term $-T\Delta S°$ is similar in magnitude but opposite in sign ($\Delta S° = -4.8$ to -6.2 cal mol^{-1} K^{-1}). Obviously, the loss of aromaticity accompanying this shift of the tautomeric equilibrium towards the quinone form in EtOH is offset by the better solvation of the *b* tautomer (*ca.* 2 kcal mol^{-1} according to the *ab initio* PCM calculations). (iv) *Ab initio* (HF/6-31G** and HF/6-311G**) calculations support the experimental results. Semiempirical methods (AM1 and PM3) appear to be less suited to treat the tautomeric properties of these types of compounds.

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