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Tautomerism in 1-phenylazo-4-naphthols: Experimental results vs quantum-chemical predictions

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ABSTRACT

The reliability in the description of the tautomerism of 1-phenylazo-4-naphthol by using of HF and MP2 ab initio levels of theory and DFT methods with variety of pure GGA (OLYP), hybrid (B3LYP and B3PW91), long range corrected (LC-BLYP) and double-hybrid (B2PLYP and mPW2PLYP) functionals with large number of basis sets was estimated. In this evaluation three criteria were used: reproduction of the bond lengths in the structures of the individual tautomers, description of the non-planarity of the enol tautomer and prediction of the position of the tautomeric equilibrium (ΔG value) at 298 K. The results show that in substantial number of cases HF reasonably covers all requirements. The tested pure (OLYP) and hybrid functionals (B3LYP and B3PW91) fail in the prediction of the position of the equilibrium independent on the basis set. The situation is slightly better at the long range corrected functional (LC-BLYP), which give predominance of the enol tautomer at 6-31+G** and D95++**. The double hybrid functionals give very good description with D95++** basis set, but at substantial computational costs.

1. Introduction

Quantum-chemical calculations are a very suitable tool to study the tautomeric compounds, but the results always remain captive on the level of theory and basis set used [1,2]. This is especially true for the description of systems, where the tautomers co-exist in solution. In order to create a solid base for theoretical investigation of the proton transfer mechanism and the effects of the environment quantum chemists need for a start to have correct description of the stationary keto/enol tautomeric ratio.

The tautomerism in 1-phenylazo-4-naphthol (**1**, Scheme 1) is one of the first discovered more than 120 years ago in a pure chemical manner [3]. It is well known that in solution **1** always exists as keto-enol tautomeric mixture and the tautomeric ratio (quantitatively defined as a tautomeric constant K_T, $K_T = [K]/[E]$), is very sensitive to the solvent environment and the temperature [4,5]. In spite of the intensive spectral and theoretical investigations many questions about the effects influencing the tautomerism in azonaphthols remained unanswered, due to the impossibility to isolate the individual tautomers by switching of the equilibrium [6,7].

Only recently advanced chemometric tools for processing of spectra of tautomeric mixtures have been developed and used to study in exact, quantitative, manner the tautomerism in **1** and in related azonaphthols and Schiff bases [6,8]. This has created conditions for exact estimation of the thermodynamic parameters governing the equilibrium (entropy, enthalpy, free energy) in non-polar solvents,[1] which gives a chance for direct comparison with the quantum-chemical results avoiding the complications of theoretical description of the specific solvent effects [1,9]. Such data give unique opportunity to test the theoretical results and to look for conditions (level of theory/basis set) that correctly describe the tautomerism in **1** as a first step for finding acceptable general solution for this class of dyes.

In addition, again recently, structural conditions for controlled shift of the tautomeric equilibrium in **1** were created [10]. In compounds **2** and **3** due to the intramolecular hydrogen bonding the equilibrium is fully shifted toward the enol form and under protonation can be gradually shifted to the keto tautomer. In such

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[1] In the following discussion under non-polar solvents we understand solvents with low polarity and without abilities for specific (proton donor/proton acceptor) interactions with the individual tautomers. This means for instance that the chloroform is excluded from this category.

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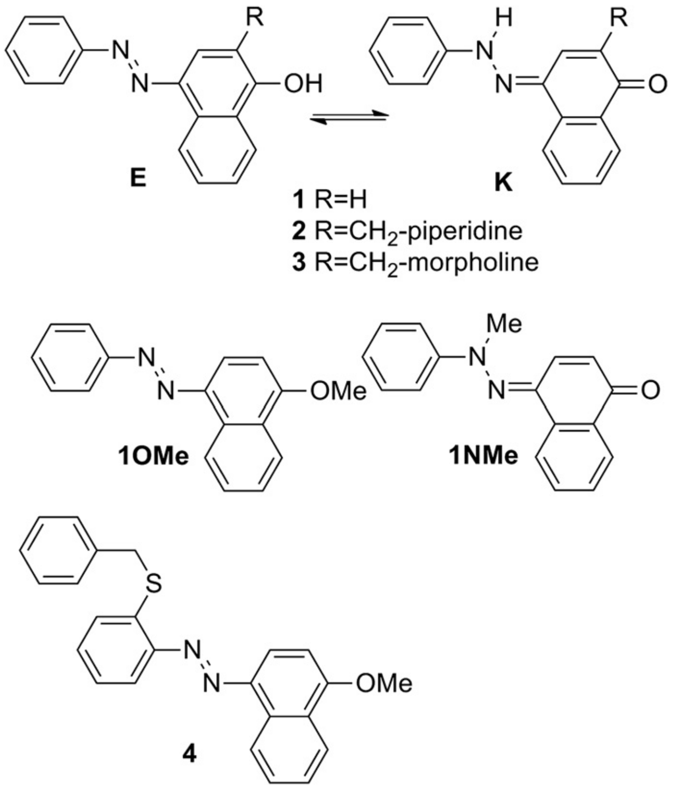

Scheme 1. Compounds under investigation.

a case the individual tautomers have been obtained for the first time in solution. The next step is to isolate them in solid state and to use the crystal structures as an additional opportunity to test the quantum chemical results.

In the current communication we report the crystal structures of the pure enol form of **1** obtained by structural modifications (**2** and **3**) and the crystal structures of the so-called model tautomers (**1OMe** and **1NMe**), where the tautomeric proton is replaced by a methyl group. It is first time when structural information for the individual tautomers of **1** is provided and this information, along with the data available in the literature for **4** [11] will be used to estimate the reliability of the individual tautomeric structures optimized by the quantum chemical calculations at various levels of theory and basis sets. In addition we will use a set of experimentally obtained tautomeric constants at room temperature in non-polar solvents in order to evaluate the theoretical predictions of the relative stabilities of the keto and enol tautomers. Although there are theoretical studies dealing with the relative stabilities of the tautomers of **1** [12], such a comprehensive study has not been performed yet. In this respect two facts have to be taken into account – the compound **1** is of size that limits the use of very sophisticated quantum-chemical methods and the lack of intramolecular hydrogen bonding[2] in the individual tautomers (**1E** and **1K**) makes this tautomeric system well defined in respect to position of the tautomeric proton and less complicated in the theoretical description of the individual tautomers.

The current work represents the extensive test of various methods (including DFT ones) for prediction of the geometry and the relative stabilities of tautomers in the studied compound. The results from the DFT calculations are extremely important due to the fact that on one side DFT methods being computationally inexpensive are very attractive, but on the other side, sometimes fail even for seemingly simple systems, as shown by Grimme [13].

However, taking into account the fact that the study is performed for one compound only, the purpose of the current communication is not to provide general answers about the most suitable level of theory and basis sets, but to initiate a discussion and to be used as a guide for further studies of larger sets of tautomeric compounds.

2. Experimental part

2.1. Synthesis

2.1.1. General

All reagents were purchased from Aldrich, Merck and Fluka and were used without any further purification. Fluka silica gel/TLC-cards 60778 with fluorescent indicator 254 nm were used for TLC chromatography and R_f-values determination. The purifications were carried out on a Biotage Horizon TM HPFC system (Charlottesville, Virginia, USA) on silica gel. The melting points were determined in capillary tubes on SRS MPA100 OptiMelt (Sunnyvale, CA, USA) automated melting point system. The NMR spectra were recorded on a Bruker Avance II+ 600 spectrometer (Rheinstetten, Germany) in deuterochloroform; the chemical shifts were quoted in ppm in δ-values against tetramethylsilane (TMS) as an internal standard and the coupling constants were calculated in Hz. The signals for the morpholine ring protons in **3** are broadened due to a slow exchange.

Compounds **1** and **2** [10], and **1OMe** and **1NMe** [14] were synthesized as described in the literature. Compound **3** was obtained from naphthalen-1-ol by applying diazo coupling/Mannich reaction sequence as a one-pot two step protocol without purification of the intermediately formed **1** as follows:

To aniline (3 mmol) ice, conc. HCl (0.9 ml), and a solution of $NaNO_2$ (3.3 mmol) in H_2O (8 ml) were subsequently added and the mixture was stirred at 0 °C for 5 min to form a diazonium salt. To a solution of naphthalene-1-ol (3 mmol) in acetone (20 ml) 10% aq. NaOH (3 ml) and then the solution of the diazonium salt were subsequently added at 0 °C. The residue formed was filtered off, washed with small portions of acetone, and dried in air to give the crude **1** [3].

To a solution of morpholine (3.3 mmol) in benzene (20 ml) paraformaldehyde (3.3 mmol), *p*-toluenesulfonic acid (20 mg), and then crude **1** (3 mmol) were added and the mixture was refluxed with stirring for 3 h. The products were partitioned between benzene and deionized water. The organic phase was dried over Na_2SO_4, and evaporated to dryness. Purification by HPFC on silica gel by using a mobile phase with a gradient of polarity from hexane to ether:hexane 50:50, yielded *4-(Phenyldiazenyl)-2-(morpholin-1-ylmethyl)naphthalen-1-ol* (**3**) in 49% overall yield: orange crystals, m.p. 158–159 °C (lit. 197–199 °C [15], protonated form); R_f- 0.56 (EtOAc:hexane 1:1); ^{1}H NMR 2.662 (bs, 4H, CH_2–N morpholine), 3.803 (bs, 4H, CH_2–O morpholine), 3.935 (s, 2H, Ar-CH_2–N), 7.447 (t, 1H, J 7.2, C*H*-4 Ph), 7.532 (t, 2H, J 7.7, C*H*-3 and C*H*-5 Ph), 7.563 (t, 1H, J 7.4, 8.2, C*H*-7 Ar), 7.643 (t, 1H, J 7.2, 8.2, C*H*-8 Ar), 7.703 (s, 1H, C*H*-3 Ar), 7.992 (d, 2H, J 7.7, C*H*-2 and C*H*-6 Ph), 8.298 (d, 1H, J 8.3, C*H*-9 Ar), 8.945 (d, 1H, J 8.5, C*H*-6 Ar), 10.844 (bs, 1H, O*H*); ^{13}C NMR 52.92 (CH$_2$–N morpholine), 61.84 (Ar-CH$_2$-N), 66.73 (CH$_2$–O morpholine), 113.25 (C_{quat}-2 Ar), 113.28 (*C*H-3 Ar), 122.12 (*C*H-9 Ar), 122.73 (*C*H-2 and *C*H-6 Ph), 122.99 (*C*H-6 Ar), 124.86 (C_{quat}-10 Ar), 125.61 (*C*H-7 Ar), 127.39 (*C*H-8 Ar), 129.08 (*C*H-3 and *C*H-5 Ph), 130.17 (*C*H-4 Ph), 132.58 (C_{quat}-5 Ar), 140.30 (C_{quat}-4 Ar), 153.29 (C_{quat}-1 Ph), 157.61 (C_{quat}-1 Ar); COSY cross peaks 2.662/3.803, 7.447/7.532, 7.532/7.992, 7.563/8.298, 7.56/7.643, 7.643/8.945; HSQC cross peaks 2.662/52.92, 3.803/66.73, 3.935/61.84, 7.447/130.17,

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[2] As it exists in the azonaphthols and Schiff bases derived from 2-naphthol for instance.