4-carboxyl-2,6-dinitrophenylazohydroxynaphthalene tautomerism theoretically re-explained

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Abstract

The tautomeric structures of 4-((2-hydroxynaphthalen-1-yl)diazenyl)-3,5-dinitrobenzoic acid have been revised by using quantum chemical (M06-2X/TZVP) calculations showing that the previously suggested structures are incorrect. By using theoretically predicted relative energies and Uv-Vis spectral analysis of a structurally similar compound (1-((2-nitrophenyl)diazenyl)naphthalen-2-ol), it has been estimated that the tautomeric equilibrium is shifted to the keto tautomer, but not completely.

Keywords: 4-((2-hydroxynaphthalen-1-yl)diazenyl)-3,5-dinitrobenzoic acid, 1-((2-nitrophenyl)diazenyl)naphthalen-2-ol, tautomerism, quantum chemistry, DFT, molecular spectroscopy

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1. Introduction

Prototropic tautomerism, defined by one of its early investigators as “the addition of a proton at one molecular site and its removal from another” [1], rearranging at the same time the system of connecting double bonds [2], is one of the most important phenomena in organic chemistry. Such systems had been called “triadic” ($\text{HX-Y=Z} \rightleftharpoons \text{X=Y-ZH}$) [3] and this early definition has more or less affected even our current understanding of this phenomenon [4], although in some cases (zwitterionic structures for instance) no clear double bond rearrangement can be observed. From the very beginning the tautomerism in azo dyes has captured a special attention, not only because 1-phenylazo-4-naphthol was one of the first tautomeric compounds described [5]. Proton exchange affects the color and stability of the dyes and therefore its investigation has substantial practical and fundamental values [6],[7],[8].

Therefore, it is not surprising that the tautomerism in azo dyes has been intensively studied both experimentally and theoretically [9],[10],[11],[12]. Although, the individual tautomers cannot be separated experimentally, their ratio can be estimated precisely by using advanced data processing of the UV-Vis spectral data [13],[14]. As a result, the availability of reliable experimental ΔG values in various solvents/temperatures has allowed benchmarking of the

theoretical methods and identification of most suitable of them, correctly describing the real tautomeric systems [15],[16] and giving the possibility for theoretical modeling of the tautomerism in the azonaphthols as a whole.

In the last several years, the synthesis of a series of 4-carboxyl-2,6-dinitrophenylazohydroxynaphthalenes has been described by Adegoke et al [17] and an intensive study of the tautomeric properties [18], solvents effects [19], sensing abilities [20] and biological activity [21] has been performed by the same group. Two are the key elements in the discussions, namely there is a tautomeric equilibrium in the studied compounds and this equilibrium is shifted towards the hydrazone tautomer. The latter is in good agreement with the effect of the strong electron acceptor substituents in the phenyl ring [7],[10] and with our observations in similar azonaphthols [22],[23]. The tautomeric structures, proposed by Adegoke and co-authors are shown in Scheme 1.

In the current communication we intend to prove that structures **1a** and **1h** do not exist in the present form. For this purpose quantum-chemical calculations and additional interpretation of already published and new experimental data will be used. It is obvious that structures **1h'** and **1h''** presented as hydrazone forms contain one (**1h'**) or two (**1h''**) hydrogen atoms more than **1a-1h** and are not tautomers of the 4-((2-hydroxynaphthalen-1-yl)diazanyl)-3,5-dinitrobenzoic acid (**1**). For this reason they will be not discussed below.

Scheme 1. Tautomerism in **1** as suggested in [17] as Figure 2 (for structures **1a** and **1h**) and in [18] as Figure 2 (for structures **1h'** and **1h''**).

2. Results and discussion

1-(Phenyldiazenyl)naphthalene-2-ol (**2**, Scheme 2) is one of the most studied tautomeric compounds due to the fact that more than 20% of the commercial dyes listed in the Color Index are based on it [24]. The suitable structural proximity makes this kind of azo naphthols very suitable ligands for forming stable metal complexes dyes [8].

Scheme 2. Tautomerism in 1-(phenyldiazenyl)naphthalen-2-ol (**2**) and nitro substituted compounds **3** and **4**.

The tautomerism in **2** has been studied by UV-Vis spectroscopy and advanced chemometrics [22], thus allowing two major conclusions to be drawn: a) the position of the tautomeric equilibrium is slightly affected by the solvent in most of the cases [25] due to the existing intramolecular hydrogen bonding; b) the effect of the substituents in the phenyl ring is the factor crucially determining which tautomer dominates [7].

From the viewpoint of organic chemistry logic, the stabilizing intramolecular hydrogen bonding should involve the β -nitrogen atom to provide a six membered ring. This structure has been proven in solution by means of NMR [13],[26] and, in addition, there is sufficient number of crystal data proving it for **2** itself [27] and for substituted compounds [28],[29],[30],[31]. In order to solve this inconsistency the stability of the structures suggested by Adegoke and co-authors (**1a** and **1h**,

Scheme 3) has been estimated theoretically against these generally accepted for this class of azo dyes, namely **1e** and **1k**. The obtained results in several solvents are summarized in Table 1. As seen, structures **1a** and **1h** are highly improbable being sufficiently less stable comparing to **1e** and **1k** respectively. Therefore it could be concluded that if tautomeric equilibrium exists in this case it includes **1e** and **1k**. According to the energy differences the equilibrium should be fully shifted to the keto tautomer **1k**, but taking into account that the used level of theory (M06-2X/TZVP and the used continuum approach together) overestimates the keto content in **2** (experimental DG value of 0.41 kcal/mol at room temperature against 0.32 kcal/mol relative energy, both in cyclohexane or *i*-octane [16]) a deeper consideration is needed.

Scheme 3. Possible tautomeric structures of **1**.

The enol form is dominating in compound **2** (67% in *i*-octane [22]), but the availability of three strong electron acceptor substituents in **1** definitely should shift the equilibrium towards the keto tautomer [7]. At the same time a careful evaluation of the spectra of **1** in various solvents (structure AZ-01 in Figures 2 and 3, [19]) shows a clear shoulder around 420 nm, which could be attributed to the enol tautomer **1e**. The published ^{13}C chemical shift (145.34 ppm, [17]) of C-*ipso* of the phenyl ring of **1** lies between the border values of ~140 ppm and ~152 ppm for the enol and keto forms in **2** like compounds, respectively, as defined by Lycka et al [32], which also suggests an incomplete shift to **1k**.

As a model of **1** we use structures **3** and **4**, which allow us to estimate the effects of the nitro groups at the *ortho* position in the phenyl ring. According to the data from Table 1, the availability of a single nitro group in **4** is almost sufficient to fully shift the equilibrium towards **4k**. It is interesting to note that in both tautomeric forms an additional intramolecular hydrogen bond is formed, but the electron acceptor effect is dominating in the stabilization of the keto tautomer. The second nitro group in **3**, due to steric hindrance with the α nitrogen atom from the azo group, has little influence being out of planarity. The absorption spectra of **3** are unknown, but as seen from Figure 1 similarity exists between the spectra of **1** shown in [19] and those of **4**.

The spectra from Figure 1 has been processed by a chemometric procedure for analysis of tautomeric systems based on resolution of overlapping bands technique [13],[14]. The absorption spectra of the pure tautomeric forms in Figure 2 show an absorption maximum for **4e** at 414 nm ($\epsilon = 21\,260\text{ l.mol}^{-1}\text{.cm}^{-1}$) and a typical resolved band for the keto tautomer with two clear maxima at 473/490 nm ($27\,100/27\,300\text{ l.mol}^{-1}\text{.cm}^{-1}$). It has been found that the content of the keto form is 60% in *i*-octane and 66% in methylene chloride, which corresponds to ΔG values at room temperature of -0.24 kcal/mol and -0.39 kcal/mol respectively. Returning back to Table 1 it is evident that M06-2X/TZVP method strongly overestimates the keto content giving a values of $\Delta E = -1.91$ kcal/mol in toluene. Taking into account the theoretical and experimental data for **2** and **4**, mentioned above, and the predicted ΔE value from Table 1, it is possible approximately the estimate the enol tautomer content in **1** as 30-31% ($\Delta G \sim 0.48\text{-}0.50$ kcal/mol) in toluene, which confirms the conclusions for predominance of **1k** coexisting with **1e**.

3. Experimental part

1-((2-nitrophenyl)diazenyl)naphthalen-2-ol (**4**) used in this study was prepared by an established procedures [33] and its purity was confirmed by TLC and m.p.

The absorption spectra were measured on a JASCO V-570 UV-Vis-NIR spectrophotometer at 25°C by using spectral grade solvents.

The quantitative analysis of the tautomeric mixture was performed by using chemometric procedure based on resolution of overlapping bands as described elsewhere [13],[14].

Quantum-chemical calculations were performed by using the Gaussian 09 D.01 program suite [34] applying M06-2X fitted hybrid meta-GGA functional [35],[36] with TZVP basis set [37]. It is worth mentioning that this method has been recently demonstrated as very suitable for describing tautomeric behavior in azonaphthols and related Schiff bases [16]. The tautomeric forms were optimized without restrictions under tight optimization conditions by using ultra-fine grid in the computation of the two-electron integrals and their derivatives. The optimized structures were then characterized as true minima by vibrational frequency calculations. For all cases, the solvent effect was described by applying the polarizable continuum model (PCM) in its integral equation formalism variant (IEFPCM) [38]. In limited cases, as identified in the text, the SMD solvation model was used [39].

4. Conclusions

It has been proven by existing crystallographic data and quantum chemical calculations that the structures of the enol and keto tautomers of 4-((2-hydroxynaphthalen-1-yl)diazenyl)-3,5-dinitrobenzoic acid as previously predicted by Adegoke are incorrect. Formation of a six-membered intramolecular hydrogen bond is the major structure stabilizing factor in the azonaphthols originating from β -naphthol.

The spectral analysis of a structurally similar compound, namely 1-((2-nitrophenyl)diazenyl)naphthalen-2-ol, shows that although the tautomeric equilibrium is shifted towards the keto tautomer, no complete transformation is observed. The same could be expected for 4-((2-hydroxynaphthalen-1-yl)diazenyl)-3,5-dinitrobenzoic acid although the theoretical calculations at M06-2X/TZVP level of theory predict very high relative stability of the keto tautomer.

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Table 1. Predicted relative energies* (kcal/mol) of the tautomers of **1**, **3** and **4** in gas phase and in selected solvents, described by using the polarizable continuum model (PCM) or SMD solvent model (in parentheses).

structure		Gas phase	Toluene	Chloroform	Acetone	Methanol
1e		2.18	2.54 (2.53)	2.75 (2.79)	2.98 (2.84)	3.01 (3.36)
1a		6.08	6.45	6.66	6.84	6.86
1k		0.00	0.00	0.00	0.00	0.00

1h		17.83	17.4	17.2	17.0	16.9
3e		1.45	1.73 (1.69)	1.91 (1.92)	2.10 (1.89)	2.12 (2.46)
3k		0.00	0.00	0.00	0.00	0.00
4e		1.50	1.91 (1.88)	2.17 (2.18)	2.45 (2.21)	2.49 (2.83)
4k		0.00	0.00	0.00	0.00	0.00

* To be comparable with the definition of the tautomeric constant ($[k]/[e]$) the relative stability must be taken as negative as sign in the discussion.

Figure 1.

Figure 2.