



4-Carboxyl-2,6-dinitrophenylazohydroxynaphthalenes 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.

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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” ($HX-Y = Z \Leftrightarrow X = Y-ZH$) [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.

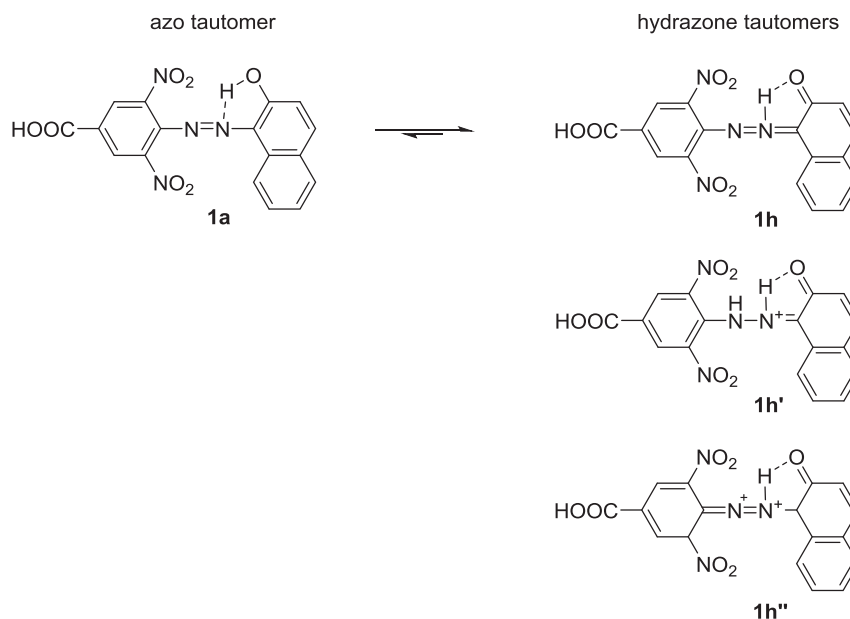
In the last several years, the synthesis of a series of 4-carboxyl-2,6-dinitrophenylazohydroxynaphthalenes has been described by Adegoke et al [17] and an intensive study of the tautomeric properties [18], solvents effects [19], sensing abilities [20] and biological activity [21] has been performed by 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

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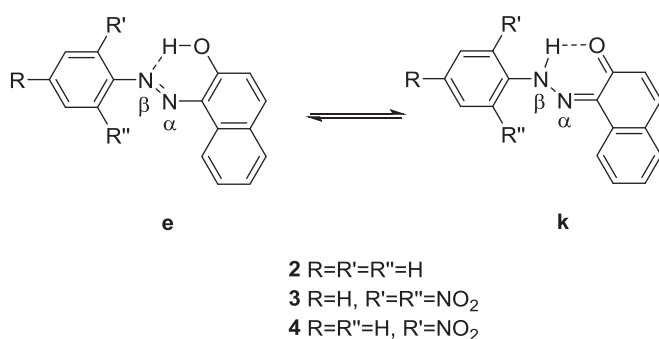
Scheme 1. Tautomerism in **1** as suggested in Ref. [17] as Fig. 2 (for structures **1a** and **1h**) and in Ref. [18] as Fig. 2 (for structures **1h'** and **1h''**).

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)diazenyl)-3,5-dinitrobenzoic acid (**1**). For this reason they will be not discussed below.

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].

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].



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

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.

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 ¹³C 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

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