Dyes and Pigments 121 (2015) 188–198

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Conformational analysis on protonation and deprotonation of calmagite in protic solvents and its reactivity through Fukui function

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ARTICLE INFO

Article history:
Received 23 March 2015
Received in revised form
16 May 2015
Accepted 18 May 2015
Available online 27 May 2015

Keywords:
DFT calculations
Calmagite
Conformational analysis
Reactivity
Protonation and deprotonation
Fukui function

ABSTRACT

In the present work a systematic theoretical study on 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid was performed. All possible protonation and deprotonation degrees were analyzed. The use of solvents in calculations affect in a direct way the stability of azo and hydrazone tautomers. This is the first systematic theoretical study, from electronic structure point of view, on this widely used azodye. Additionally, local reactivity utilizing the Fukui function was obtained. Interestingly, reactivity of the molecule undergoes no significant changes despite azo–hydrazone tautomerism, since the Fukui functions are not modified in a significant way in both tautomers. It is worth mentioning that results presented here are important in studies about degradation of this kind of azodyes, in studies when calmagite forms complex compounds with metallic and lanthanide atoms or in photoabsorption studies since spectrum depends on protonation and deprotonation degree and on the most stable conformers in the sample.

1. Introduction

Azodyes have been widely used in fields including textile dyebaths, foods, cosmetics and biological applications [1]. Owing to the importance of molecular structure, in the past years, experimental and theoretical analysis on azodyes has been performed [2–7] In azodyes with hydroxyl groups in benzene or naphtalene groups, azo–hydrazone tautomerism has received very much attention since 1883 when Liebermann et al. [8] proposed the capacity of bonding of the hydroxyl proton with a nitrogen atom of the azo group. With regard to azo–hydrazone tautomerism it has been demonstrated the relevance of the solvent [9–11], in addition, it is well known that the knowledge of structure of the dye is key to understanding its properties and reactivity [7]. Additionally, given the toxicity of azodyes, its degradation is one of the most important topics. A promising way for understanding the possible vias to degrade azodyes is a clear knowledge of their molecular structure and the reactivity of their different groups. On the other hand, the development of pH sensors continues as a great challenge today. However, for understanding the change of color with pH variation a deep analysis of molecular conformations is essential. These two important issues can be addressed from a theoretical point of view through density functional theory (DFT).

In spite of the widespread amount of theoretical studies on azodyes, there is no information, from electronic structure point of view, on 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid (calmagite), which is an azodye. This molecule was proposed by Lindstrom and Diehl [12] in 1960 as an indicator in the titration of magnesium with EDTA. Currently, this molecule is used as a sensor utilizing electrochemistry [13] or spectrophotometry [14], in fact, calmagite has been used as reagent for molybdenum determination [15] or as chelating agent with copper [16]. Since this azodye is being utilized in complex compounds its chemical reactivity understanding is crucial. On the other hand, since color of calmagite change with pH owing to deprotonation of the molecular structure, it continues being utilized as a metallochromic indicator in EDTA titrations [17]. Recently, studies of the voltammetric behavior of this molecular structure has been performed where the effect of pH on the reduction peaks has been analyzed and the electrochemical reaction mechanism of the azo compound has been suggested [18].

Calmagite is a triprotic acid composed of a sulfonic acid and two hydroxyl groups whose protons are removed from the molecular structure through pH variation. Sulfonic acid is easily deprotonated

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http://dx.doi.org/10.1016/j.dyepig.2015.05.022
0143-7208/

in water, whereas the hydroxyl groups have two successive acid dissociation constants at 8.2 and 12.4 according to [19] or 7.95 and 12.05 according to [20]. It is worth to mention that the most of the studies are concerned with deprotonation of the molecular structure, however, when pH is lower there are some sites in calmagite where protons could be added, and at this point, a theoretical study is important to analyze all the possibilities of not only deprotonation but also protonation.

Calmagite is shown in Figs. 1 and 2, as one can observe, there are three protons where the molecule can be potentially deprotonated, then, three mono-deprotonated molecules (at H1, H2 or H3) could be proposed in order to get the sequence of deprotonation. Furthermore, for di-deprotonated calmagite, there are three possibilities H1 and H2, H1 and H3 and finally, H2 and H3, importantly, it is expected that the latter configuration should be the most unstable because H1 is expected to be the first proton removed. In addition, for each configuration in mono- and di-deprotonated calmagite, hydrazone tautomers may be present in the experiment. At the end, calmagite without three protons is performed. Previous work [12,20,19] mentioned that deprotonation is achieved, however, there is no information about the protonation, which is a possibility, therefore, in order to get a better understanding, protonation is also analyzed. This analysis is important owing to that protonation could be possible at lower pH. First of all, calmagite protonated at H1, H2 and H3 is proposed, nonetheless, it is well known H1 proton is easily removed, thus one may consider a structure where the H1 proton is removed and adding a proton at N1 or N2, keeping a neutral charge in the molecular structure. In addition, for the first protonation it could be considered a proton at N1 or at N2. Finally, the calmagite could be twice protonated, one proton at N1 and the other at N2.

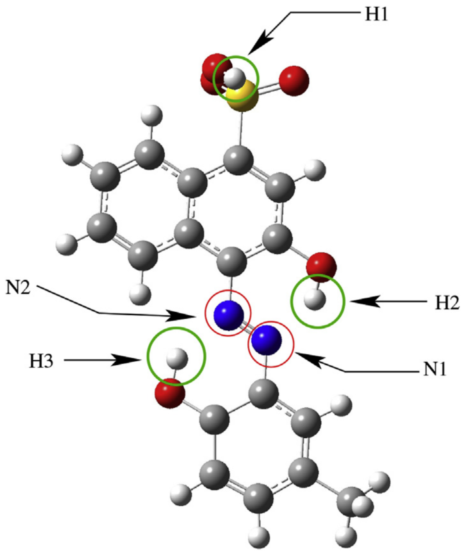
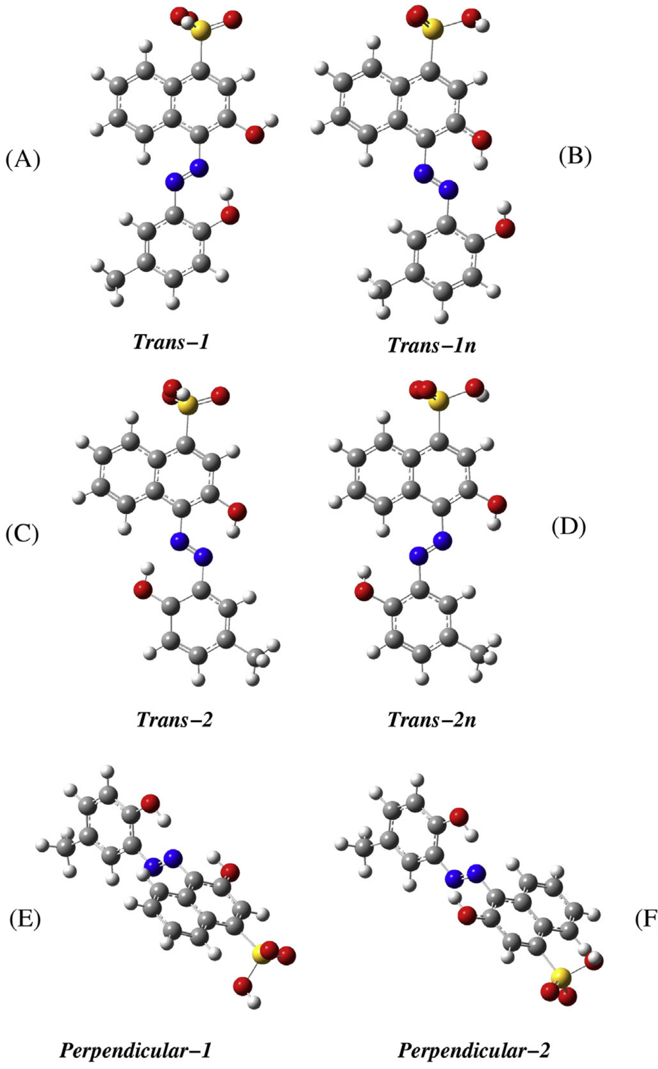


Fig. 2. Protons nomenclature.



Trans−1 *Trans−1n*

Trans−2 *Trans−2n*

Perpendicular−1 *Perpendicular−2*

Fig. 1. Initial isomers for calmagite.

The most stable conformers of calmagite at each protonation a deprotonation degree were obtained, finding that the inclusion of solvent in calculations involving this molecular structure plays a crucial role in order to stabilize the azo, hydrazone or both conformers. In addition, the use of solvent is very important when reactivity of calmagite is determined.

The present work is organized as follows: In the next section theoretical methodology utilized here is presented. Later, results about conformational analysis on protonation and deprotonation, as well as its discussion is performed, continuing with the presentation of calmagite reactivity through Fukui function. Finally, summary and conclusions are given.

2. Method of calculations

As initial structures, several proposals were done; in Fig. 1 the different isomers are shown. In (A) and (B) *Trans-1* isomers are shown, in (C) and (D) *Trans-2* isomers are shown, the difference between (A) and (B) or between (C) and (D) is the orientation of the azo group ($R-N=N-R'$), in (E) and (F) two perpendicular positions between the naphthalene and benzene group are shown. It is well known that azobenzenes, which are azodyes, present *cis*−*trans* isomerization, therefore, taking into account this kind of equilibrium, also the *cis* isomer of calmagite was proposed for optimization, however, calculation was never converged (optimized) owing to steric effects. For azobenzenes there is no steric repulsion between benzenes because of the separation among benzene groups and this is the reason why in azobenzenes *cis* isomer can be converged, however, calmagite has a naphthalene and a benzene group causing steric repulsion between these groups. Then, *cis* isomer was not proposed for calmagite isomerization. In order to simulate the pH variation, for each of these isomers, protonation degree was varied, it is, from the original structure (Fig. 1) a