Two Acid Forms of Dimethylaminoazobenzene

Dyes Studied by Density Functional Theory

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Abstract

The ultraviolet/visible spectra of dimethylaminoazobenzene dyes in aqueous solution often show a clear shoulder on the long wavelength side of the principal absorption. These shoulder was traditionally explained by the interaction between the azo group and the solvent molecules. However this model is insufficient to explain the shoulder of acid form of methyl red (MR). Based on the calculation using the density functional theory and the time-dependent density functional theory, we attributed the observed spectra to the two overlapping bands of the two differently protonated dyes. For MR in solvents of lower dielectric constants the carboxylate ion is suggested to be protonated prior to the azo group. Our calculation support this suggestion and we consider that this is why the shoulder absorption does not appear for MR in solvents of lower dielectric constants. We consider that Methyl Yellow and Methyl Orange also exist as the mixture of two differently protonated dyes.

Keywords: dimethylaminoazobenzene, acid-base equilibria, UV/Vis spectrum, DFT calculation

1 Introduction

The reaction of Azobenzene dyes are often influenced by the protonation of
the azo group. For example, they are well known photoswitches and their cis to trans isomerization proceed faster in acidic solution [1]. The protonation of the azo group also changes the color of dyes. Dimethylaminoazobenzene dyes are often used as pH indicators.

The ultraviolet/visible (UV/Vis) spectra of these dimethylaminoazobenzene dyes in acid aqueous solution show a clear shoulder on the long wavelength side of the principal absorption [2]. However the shoulder doesn’t appear in the spectra of Methyl Red (MR) in solvents of lower dielectric constants (Figure 1).

![UV/Vis spectrum of Methyl Red](image)

**Fig. 1 UV/Vis spectrum of Methyl Red (a) In 1-Octanol (b) In the water**

Usually this shoulder is explained by the interaction between the azo group and the solvent molecules [2-4]. The long-wavelength component is considered to have a hydrogen-bonding interaction between the solvent and the azo nitrogen group, while the short-wavelength component does not have it. The protonation of the azo group gives a pronounced red shift of the $\pi \rightarrow \pi^*$ transition. For example the absorption peaks of MR_IN and MR_HIN are 423 nm and 522 nm in the water, respectively [2]. (We shows the species involved in the acid-base equilibria of MR in Scheme 1 [2, 5].) Therefore, the hydrogen-bonding between dyes like MR_IN and a water molecule would give a smaller red shift than the protonation. However, this model is insufficient to explain the shoulder of MR_HIN in the water. The absorption peaks of HIN and H2IN appear at almost the same position (522 nm and 513 nm in the water, respectively [2]). The hydrogen-bonding between MR_HIN(a) and a water molecule seems not to give a large red shift.
Two acid forms of dimethylaminoazobenzene dyes studied

In pure water the N=N group of MR is more basic than the COO⁻ group and protonate first (MR_HIN(a)) [6]. Drummond et al. [2] inferred that the basicity of these groups depend on the dielectric constant of the solvent and in solvents of lower dielectric constants the COO⁻ group protonate first (MR_HIN(b)). Their original form of MR_HIN(b) in their report has no intramolecular hydrogen bonding. However Ross et al. reported that MR has an intramolecular hydrogen bonding in the carbon tetrachloride [5]. Therefore, we added the bonding to the form of MR_HIN(b) (Scheme 1). The structure of MR_HIN(b) with the intramolecular hydrogen bonding is similar to that of MR_HIN(a). However, the spectrum of MR_HIN(b) shows no shoulder while MR_HIN(a) shows that.

In the following, we will discuss the cause of the shoulder absorption of MR and clarify why it disappear in solvents of lower dielectric constants by performing DFT and TDDFT calculations.

2 Computational details

The geometries were calculated using DFT employing the hybrid B3LYP xc-functional and the 6-31+G(d) basis set using WinGamess (32 bit, ver. 11) [7]. The excited states were calculated employing TDDFT with the B3LYP/6-31+G(d) and CAMB3LYP/6-31+G(d). In the calculation, the solvent effects were included using the continuum C-PCM solvation model. We calculated the geometry and
absorption wavelength of MR in solvents of lower dielectric constants with constants defining cyclohexane. The result was analyzed using Winmoster [8].

3 Results and discussions

First, we optimized the geometry of MR_HIN(a), (c). The optimized structural parameters of HIN(a) were agreed with the experimental data [9]. Drummond et al. [2] suggested when MR is dissolved in solvents of lower dielectric constants, the carboxylate ion group becomes more basic than the azo group and MR_HIN(b) is formed. The change of basicity is reproduced in the optimized structural parameters. The distance between the hydrogen of COOH and N=N is 1.641 Å in the water and has a larger value 1.690 Å in cyclohexane. And the distance between the hydrogen of COOH and the oxygen of COOH is 1.015 Å in the water and has a smaller value 1.004 Å in cyclohexane. These results show that the hydrogen is attracted by N=N more strongly when it is in the water than when it is in solvents of lower dielectric constants.

We also calculated the absorption spectra of them by TDDFT (Table 1). TDDFT errors are expected to be within the accepted accuracy of 0.2 - 0.3 eV, in the case of B3LYP [10, 11]. The principal absorptions of MR were reproduced. However, the absorption shoulder at about 550 nm was not reproduced.

Then, what is the origin of the shoulder? To clarify it, we first examined the parameters of IN. The atomic charge is calculated by two method (Löwdin and Mulliken). To avoid confusion, here we call the benzene ring with the COOH as ring-C, and that with the NMe₂ as ring-N. Also, we call the nitrogen atom of the azo nitrogen next to the ring-C as Nc, and that next to the ring-N as Nn (Scheme 2.). The atomic charge of Nc of IN seems to be more negative than that of Nn because of the quinoidal resonant component (Scheme 1, MR_IN-(2)). But our calculation shows that the atomic charge of Nn is as negative as that of Nc (Löwdin), or more negative than that of Nc (Mulliken) (Table 2).

We optimized the geometry of MR_HIN(c) (Scheme 2). The calculated principal absorption of MR_HIN(c) was at 502.5nm (Table 1), which agreed with the wavelength of the shoulder within the accepted accuracy of 0.2 - 0.3 eV. We also verified by calculating the harmonic force constants, the structure of MR_HIN(c) is a minimum, at least in the water. Therefore, we consider that the shoulder is originated from MR_HIN(c).
Table 1 Absorption wavelengths of methyl red's in solutions

<table>
<thead>
<tr>
<th></th>
<th>experiment</th>
<th>calculation(B3LYP)</th>
<th>calculation(CAMB3LYP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ(nm)</td>
<td>λ(nm)</td>
<td>λ(nm)</td>
</tr>
<tr>
<td></td>
<td>E=hc/λ(eV)</td>
<td></td>
<td>E=hc/λ(eV)</td>
</tr>
<tr>
<td>IN</td>
<td>423(nm)</td>
<td>464.6(nm)</td>
<td>433.9</td>
</tr>
<tr>
<td></td>
<td>(2.931eV)</td>
<td>(2.669(eV))</td>
<td>(2.858eV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.14</td>
<td>0.846</td>
</tr>
<tr>
<td>HIN</td>
<td>468.1(nm)</td>
<td>2.649(eV)</td>
<td>481.9(nm)</td>
</tr>
<tr>
<td>(a)</td>
<td>522(nm)</td>
<td>2.375(eV)</td>
<td>2.573(eV)</td>
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<tr>
<td></td>
<td>(2.118eV)</td>
<td>0.038</td>
<td>1.0891</td>
</tr>
<tr>
<td></td>
<td>ca.550(nm)</td>
<td>2.254(eV)</td>
<td>413.5(nm)</td>
</tr>
<tr>
<td>(c)</td>
<td>502.5(nm)</td>
<td>2.468(eV)</td>
<td>2.999(eV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.06</td>
<td>0.1221</td>
</tr>
<tr>
<td>HIN</td>
<td>490(nm)</td>
<td>2.530(eV) (*2)</td>
<td>458.1(nm)</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td></td>
<td>2.707(eV) (*3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.829</td>
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</tr>
</tbody>
</table>

(*) Reference 2 (In the water)  (*2) Reference 9 (In EtOH)  (*3) In cyclohexane

Table 2 Atomic charges of Nn, Nc of methyl red in water

<table>
<thead>
<tr>
<th></th>
<th>IN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mulliken</td>
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<tr>
<td>Nn</td>
<td>-0.148</td>
</tr>
<tr>
<td>Nc</td>
<td>-0.079</td>
</tr>
<tr>
<td>Löwdin</td>
<td></td>
</tr>
<tr>
<td>Nn</td>
<td>-0.156</td>
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<tr>
<td>Nc</td>
<td>-0.164</td>
</tr>
</tbody>
</table>

Scheme 2 Structure of IN and HIN(c)

There is a research paper that reports, for a series of trans-azobenzene derivatives, B3LYP provide excitation energies close to the experimental values [12]. However, TDDFT often suffer from incorrect description of charge-transfer states when hybrid functionals such as B3LYP are used. Therefore, we carried out TDDFT calculations with long-range corrected functional CAM-B3LYP, and verified the result that the wavelength of the absorption peak of MR_HIN(c) was longer than that of MR_HIN(a) (Table 1).
The calculated electronic energy of MR_HIN(c) is higher than that of MR_HIN(a) by 16.9 (kcal/mol) in the water. However, c-PCM solution model does not include the effect of hydrogen bonding. MR_HIN(c) would be more stabilized by the solvation in the water. We consider that HIN is mostly in the form of MR_HIN(a), although MR_HIN(a) and MR_HIN(c) exist simultaneously in the thermal equilibrium. In addition, in solvents of lower dielectric constants, MR_HIN(c) can’t be created because the carboxylate ion is protonated prior to the azo group.

Why the peak absorption wavelength of MR_HIN(c) is longer than that of MR_HIN(a)? We compared the calculated bond lengths of MR forms in the water. MR has a canonical form which has N-N=Ph (Ring-N) such as MR_IN-(2). The contribution of this form to the resonance hybrid was examined by the bond length of N-N and N=Ph (Ring-N). The bond length of N=N became longer in the order of MR_IN, MR_HIN(c), MR_HIN(a), and the bond length of Nn-Ph (Ring-N) became shorter in the order of MR_IN, MR_HIN(c), MR_HIN(a). Thus, the contribution of the canonical form like MR_IN-(2) increases by the bonding between H and N=N, and the contribution is larger when the H+ bonds to Nc than that when the H+ bonds to Nn. Now, azo group can also make a canonical form which has N-N=Ph (Ring-C). The bond length of Nc-Ph (Ring-C) is 1.421 Å, and that of Nn-Ph (Ring-N) is 1.401 Å for IN. Thus the contribution of canonical form with N-N=Ph (Ring-C) is smaller than that of the canonical form with N-N=Ph (Ring-N) for IN. The bond length of Nc-Ph (Ring-C) becomes shorter in the order of MR_IN, MR_HIN(a), MR_HIN(c). We consider that the contribution of the canonical form with N-N=Ph (Ring-C) is larger for MR_HIN(c), and causes the red shift of the absorption peak.

Methyl Yellow (4-dimethylaminoazobenzene) and Methyl Orange (sodium 4-[4′-(dimethylamino) phenylazo]-benzenesulfonate) also show the shoulder absorption in acidic aqueous solution [2]. However, in the case of MR in solvents of lower dielectric constants, the carboxylate ion group is protonated first, and MR_HIN(c) would not be created. We consider that Methyl Yellow and Methyl Orange also exist as the mixture of two differently protonated dyes.

3 Summary

The spectra of the acid form of dimethylaminoazobenzene dyes often have a clear shoulder on the long wavelength side of the principal absorption. We performed DFT and TDDFT calculations employing the B3LYP/ 6-31+G(d) with C-PCM solvation model and inferred that this shoulder is due to the acid form HIN(c) created by the protonation of Nn. By adding a dimethylamino group (auxochrome) to azobenzene, and the wavelength of the peak absorption becomes longer (320nm [13] → 423nm [2]). The protonation of Nc increases the contribution of the canonical form which has N-N=Ph (Ring-N) (HIN(a) in Scheme 1) and the wavelength of the peak absorption becomes more longer (423nm
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→ 522 nm) [2]. Moreover, the protonation of Nn increases the contribution of the canonical form which has N-N=Ph (Ring-C) (HIN(c) in Scheme 2) and the wavelength of the peak absorption becomes much longer (423nm → ~550 nm).

However, for MR the calculated electronic energy of HIN(c) form is higher than that of MR_HIN(a). In the water, HIN is considered to be mostly in the form of MR_HIN(a) and the absorption of HIN(c) appear as a shoulder of the principal absorption. The acid form of Methyl Yellow and Methyl Orange in the water also shows similar overlapping spectrum. We consider they also exist as the mixture of two differently protonated dyes. When MR is dissolved in solvents of lower dielectric constants, the carboxylate ion is protonated prior to the azo group and the shoulder absorption does not appear.

References


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