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# Tautomeric Equilibrium in 1-Phenylazo-2-Naphthol— A Quantitative Study

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## *ABSTRACT*

*A new approach for quantitative analysis of the tautomeric azo–quinonehydrazone equilibria was applied to 1-phenylazo-2-naphthols. The spectral characteristics of both tautomeric forms were calculated from the absorption spectra, taking into account the solvent polarity. Using the PPP–MO method, the calculated electronic transitions for both tautomeric structures were compared with the corresponding experimental values.*

## INTRODUCTION

Arylazo derivatives of naphthols can exist either as hydroxyazo compounds or as quinonehydrazone, as typified by $I_A$ and $I_H$ in Scheme 1.

Both tautomeric forms A and H exist in equilibrium and the tautomeric constant $K_T$ = [H]/[A] depends upon the environment and substituents.[1–7] For the 1-phenylazo-2-naphthols and 2-phenylazo-1-naphthols, the situation is particularly interesting since the existence of internal hydrogen bonding leads to additional stabilization of the tautomeric equilibrium towards external influences such as solvent environment and the presence of substituents of different nature.[5,8–10] In the case of 1-phenylazo-4-naphthols such stabilization is not possible and the equilibrium $I_A \rightleftarrows I_H$ is more responsive to external influences.[1,3–6,11]

Statistical evaluation of the commercially disclosed structures[4] of azo dyes in the Colour Index revealed that about 50% of them contain naphthol ring system. However, lack of knowledge of the molar

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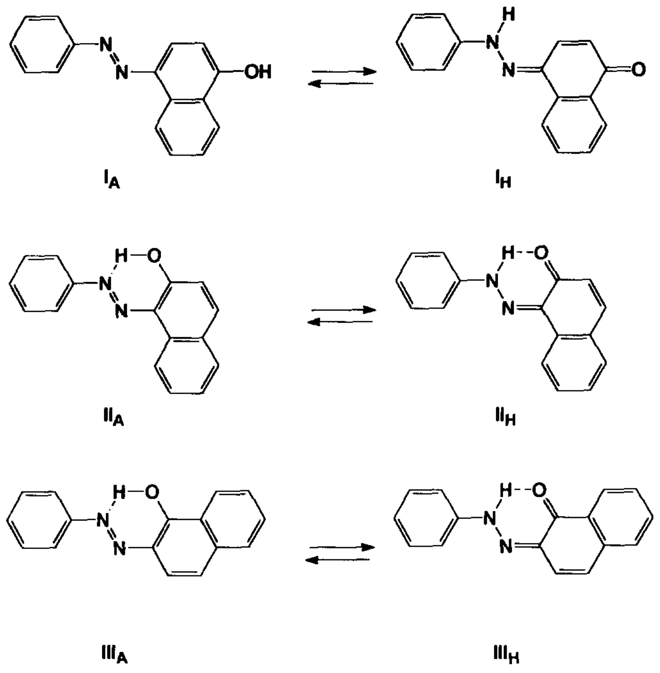

Scheme 1

absorptivities of the individual tautomeric forms means that the quantitative values for $K_T$ cannot be obtained directly; semiquantitative approaches, based on various assumptions and approximations, are usually used.[1,9–15]

In previous studies,[11,16–18] two different approaches for quantitative analysis of tautomeric equilibria were proposed and tested in the case of $I_A \leftrightarrows I_H$. The aim of the present study is to apply this new quantitative approach[16–18] in determining the tautomeric equilibrium constant $K_T$, and the individual spectral characteristics of the pure tautomeric forms of 1-phenylazo-2-naphthol in different solvents. It should be noted that molecules of this type, in solution or in the solid state, can show a wide variety of interactions, including azo–quinonehydrazone tautomerism, inter- and intramolecular hydrogen bonding, aggregation and acid–base indicator behavior, each of which may significantly alter the technologically important light absorption properties.

## MATERIALS AND METHODS

1-Phenylazo-2-naphthol (II) used in this study was prepared by established procedures[1] and its purity was confirmed by TLC and m.p.

The absorption spectra were measured on a Perkin-Elmer Lambda 17, using spectral grade solvents.

The quantitative spectral analysis was carried out as previously described.[16,19,20]

The quantum chemical calculations were carried out using a conventional PPP–SCF–CI program; the relevant parameters used were those used by Griffiths *et al.*[21–23]

## RESULTS AND DISCUSSION

Changes in the absorption spectra of **II** with the changes in the water volume content in the isomolar solvent system ethanol/water are shown in Fig. 1. The second derivative ($d^2A/d\nu^2$) spectra[20] of the initial and final isomolar solutions are given in Fig. 2. These changes are less pronounced than in the case of 1-phenylazo-4-naphthol,[11,16–18] due to the existence of intramolecular hydrogen bonding in **II**, leading to significant uncertainties in finding individual absorption areas for both of the tautomeric forms, and difficulties in applying the classical two component analysis.[11]

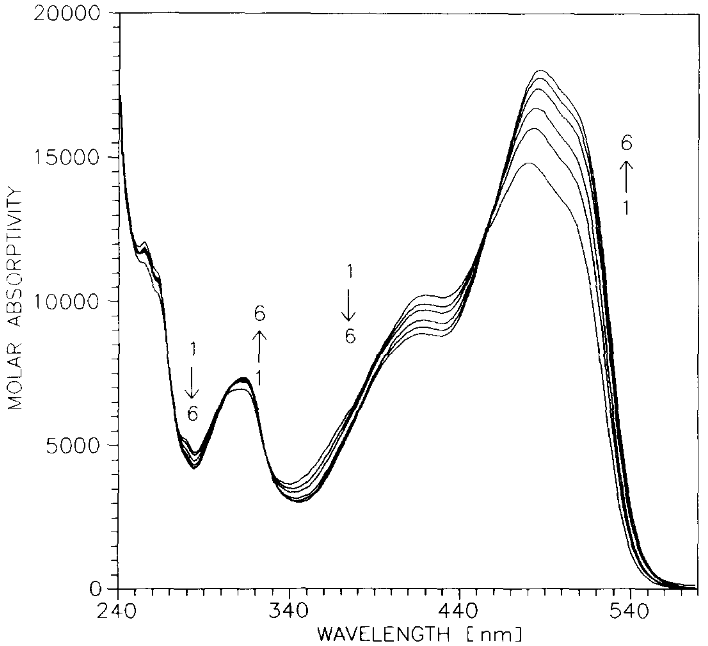

**Fig. 1.** Absorption spectra of **II** in different volume ratios of ethanol/water. The percentage of water for curves 1–6 is given in Table 2.

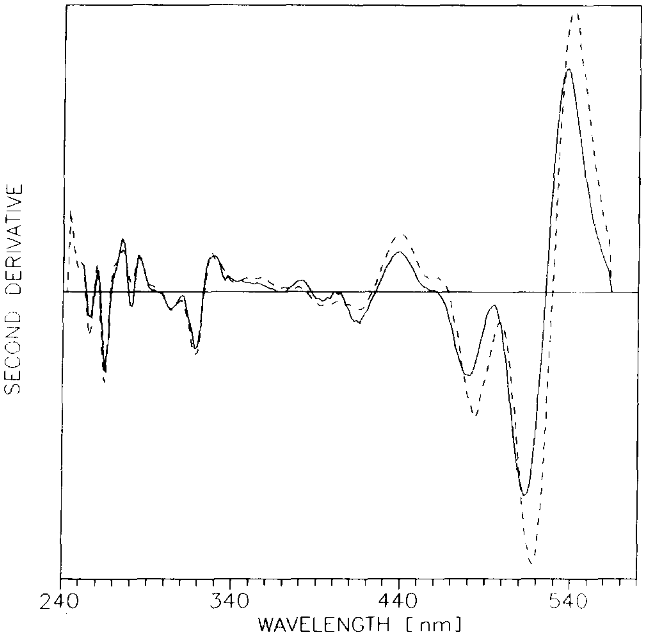

**Fig. 2.** Second derivative ($d^2A/d\nu^2$) spectra of 1 (——) and 6 (- - - -).

According to our approach,[16–18] each absorption spectrum in Fig. 1 is resolved into individual bands[19,20] and each band is assigned to a particular tautomeric form. In Table 1, the position and integral intensities[17,19,20] of the resolved individual bands are presented. The assignment of each band in Table 1 is made according to the following principle:

> The increase of the content of a particular tautomeric form leads to an increase of the integral intensities of the individual bands composing its absorption spectrum, and vice versa.

The absorption spectra of 1-phenylazo-2-naphthol in ethanol and in ethanol/water = 40/60%, together with the resolved individual spectra, are shown in Fig. 3.

The results obtained for the molar parts $X_A$ and $X_H$, and also those for the tautomeric constant $K_T$, are given in Table 2.

It should be noted that the values of the standard deviations (Table 2) are less than 1%, suggesting that the use of the current approach is correct.

The absorption spectra of **II** in the solvent systems i-octane/dichloromethane, methanol/formamide, and tetrachloromethane/chloroform, were analyzed in a similar way, and the results obtained for the values of $X_A$, $X_H$ and $K_T$, together with the corresponding dielectric constants ($D$) of the pure solvents used, are summarized in Table 3.

**TABLE 1**

Position and Integral Intensities[a] of the Resolved Individual Gaussian Bands for Each Absorption Spectrum of **II** in Ethanol/Water ($c_0 = 6{\cdot}984 \times 10^{-5}$ mol l$^{-1}$, $l = 1$ cm)

| *Band* | | *Solution (% of water)* | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | *1* *(0%)* | *2* *(10%)* | *3* *(20%)* | *4* *(40%)* | *5* *(50%)* | *6* *(60%)* | |
| 1 | $\lambda_{max}$ | 220·6 | 220·5 | 220·1 | 219·7 | 219·4 | 219·3 | H |
| | *I* | 20118 | 20271 | 21280 | 22061 | 23562 | 24118 | |
| 2 | $\lambda_{max}$ | 257·4 | 257·2 | 256·9 | 256·7 | 256·7 | 256·7 | H |
| | *I* | 1682 | 1734 | 1843 | 1926 | 2091 | 2179 | |
| 3 | $\lambda_{max}$ | 265·7 | 265·6 | 265·6 | 265·4 | 265·3 | 265·3 | A |
| | *I* | 107 | 104 | 93 | 88 | 83 | 78 | |
| 4 | $\lambda_{max}$ | 276·1 | 274·8 | 273·9 | 272·3 | 272·3 | 271·7 | H |
| | *I* | 976 | 991 | 1126 | 1120 | 1271 | 1292 | |
| 5 | $\lambda_{max}$ | 305·3 | 305·7 | 306·4 | 306·6 | 307·1 | 307·2 | H |
| | *I* | 1057 | 1102 | 1089 | 1054 | 1053 | 1076 | |
| 6 | $\lambda_{max}$ | 317·9 | 317·8 | 317·8 | 317·8 | 317·8 | 317·8 | H |
| | *I* | 102 | 111 | 112 | 125 | 118 | 120 | |
| 7 | $\lambda_{max}$ | 343·7 | 344·8 | 345·8 | 349·1 | 348·0 | 348·0 | A |
| | *I* | 2124 | 2226 | 2093 | 2317 | 1949 | 1956 | |
| 8 | $\lambda_{max}$ | 386·9 | 386·4 | 385·9 | 384·6 | 383·6 | 383·2 | A |
| | *I* | 1038 | 924 | 867 | 689 | 676 | 636 | |
| 9 | $\lambda_{max}$ | 391·8 | 392·3 | 393·0 | 395·3 | 394·4 | 394·6 | H |
| | *I* | 33 | 40 | 53 | 94 | 112 | 141 | |
| 10 | $\lambda_{max}$ | 420·4 | 420·0 | 419·5 | 418·9 | 418·0 | 417·9 | A |
| | *I* | 1287 | 1244 | 1209 | 1105 | 1078 | 1041 | |
| 11 | $\lambda_{max}$ | 459·9 | 461·1 | 461·4 | 461·9 | 461·5 | 461·8 | H |
| | *I* | 1410 | 1509 | 1599 | 1627 | 1728 | 1740 | |
| 12 | $\lambda_{max}$ | 489·6 | 491·2 | 491·9 | 492·8 | 493·3 | 493·7 | H |
| | *I* | 1367 | 1483 | 1568 | 1619 | 1740 | 1778 | |
| 13 | $\lambda_{max}$ | 514·2 | 515·6 | 516·3 | 517·3 | 517·8 | 518·3 | H |
| | *I* | 499 | 532 | 552 | 572 | 562 | 573 | |

[a] $I = 1{\cdot}063 \times A_{max} \times \Delta\nu_{1/2}$.[19]

According to the order of increasing values of $K_T$, i.e. the increase of the H-form, the solvents investigated can be placed in the following order: i-octane < tetrachloromethane < ethanol < dichloromethane < chloroform < methanol < formamide.

In general, there is no clear correlation between the empirical parameters reflecting the solvent polarity[24,25] and the position of the tautomeric equilibrium. In non-polar solvents such as i-octane and tetrachloromethane, the A-form predominates, whilst in more polar solvents such as formamide, the opposite holds true. As in the case of **I**[11] two factors are responsible for this tautomeric shift, i.e.

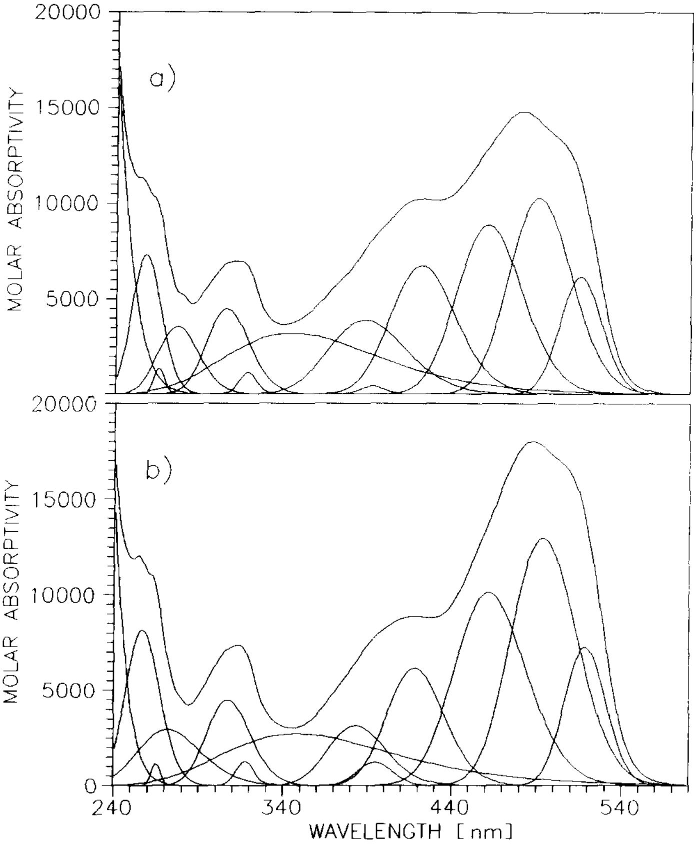

**Fig. 3.** Absorption spectra of **II** in (a) 100% ethanol and (b) ethanol/water = 40/60% with resolved individual bands.

(a) selective solvation, depending on the two- and three-dimensional structure of the solvent;[24,26]
(b) the ability of the solvent to form stronger intermolecular H-bonds with a particular tautomeric form.

In this respect, the stabilization of a given tautomer could be associated with the way in which the solvent molecules order themselves around the dye, for minimum energy of the system. However, both factors favor the more polar ($\mathbf{II}_H$) form, suggesting that its intramolecular hydrogen bond is stronger than those in $\mathbf{II}_A$.

The absorption spectra of the individual tautomeric A- and H-forms of **II** in ethanol, i-octane and tetrachloromethane, calculated according to ref. 17 are shown in Fig. 4.

It is evident from Fig. 4 that the molar absorptivities relationship

TABLE 2
Values of $X_A$, $X_H$ and $K_T$ for Each Isomolar Solution of **II** in Ethanol/Water

| *No.* | *Water (%)* | $X_A$ *(%)* | $X_H$ *(%)* | $K_T$ | *Standard deviation of* $X_A$ *(%)* |
|---|---|---|---|---|---|
| 1 | 0 | 58·0 | 42·0 | 0·724 | 0·08 |
| 2 | 10 | 55·7 | 44·3 | 0·795 | 0·08 |
| 3 | 20 | 53·2 | 46·8 | 0·879 | 0·07 |
| 4 | 40 | 51·2 | 48·8 | 0·953 | 0·09 |
| 5 | 50 | 47·8 | 52·2 | 1·092 | 0·09 |
| 6 | 60 | 46·7 | 53·3 | 1·141 | 0·10 |

$\varepsilon_H(\lambda_H)/\varepsilon_A(\lambda_A)$ is about two, which is the principal reason why the semi-quantitative evaluations of $X_H$ and $K_T$[7,10] are higher than those given in Tables 2 and 3, in accord with the calculated values of Morgan[27] from the IR spectra of **I** and **II** in chloroform, who noted that the observed UV–vis spectra overestimate the amount of $\mathbf{II}_H$ present.

These findings provide an opportunity to use the quantum chemical PPP–MO approach for the interpretation of the electronic transitions and $\pi$-electronic structure of the azo and hydrazone tautomeric forms, allow a prediction to be made of their spectroscopic differences, and permit suggestions to be made about the important characteristics of the tautomeric structures which determine their coloristic properties. The calculated values of $\lambda_{max}$ and oscillator strengths $f$ for both tautomeric forms $\mathbf{II}_A$ and $\mathbf{II}_H$ are compared in Table 4 with the corresponding values of $\lambda_{max}$ and $f$ in tetrachloromethane.

The calculated electronic transitions for both tautomeric forms correspond very closely to the experimental data. As Griffiths[21] has

TABLE 3
Values of $X_A$, $X_H$ and $K_T$ for **II** in Different Solvents

| *Solvent* | $X_A$ *(%)* | $X_H$ *(%)* | $K_T$ | *D* |
|---|---|---|---|---|
| i-Octane | 66·9 | 33·1 | 0·494 | 1·94 |
| Tetrachloromethane | 64·1 | 35·9 | 0·560 | 2·23 |
| Chloroform | 40·6 | 59·5 | 1·463 | 4·7 |
| Dichloromethane | 54·4 | 45·6 | 0·838 | 8·9 |
| Ethanol | 58·0 | 42·0 | 0·724 | 24·3 |
| Methanol | 39·2 | 60·8 | 1·551 | 32·6 |
| Formamide | 26·2 | 73·8 | 2·816 | 110·0 |

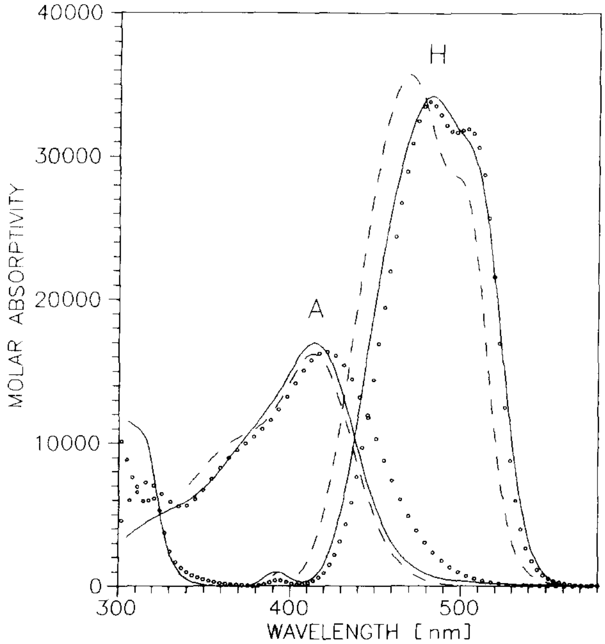

**Fig. 4.** Individual absorption curves of both tautomeric forms of **II** in ethanol (——); i-octane (– – – –) and tetrachloromethane (·······).

### TABLE 4

Comparison Between the Calculated (PPP–MO) Electronic Transitions with their $f$ Values, and the Individually Resolved Gaussian Absorption Bands for Both of the Tautomeric Forms of **II** in Tetrachloromethane

| *Form* | $\lambda_{max}^{calc}$ *(nm)* | $f^{calc}$ | $\lambda_{max}^{exp}$ *(nm)* | $f^{exp\ a}$ | |
|---|---|---|---|---|---|
| A | 429 | 0·765 | 426 | 0·228 | 0·412 |
| | | | 371 | 0·184 | |
| | 329 | 0·244 | 314 | 0·109 | |
| | 293 | 0·008 | | | |
| | 288 | 0·008 | 280 | 0·016 | |
| | 279 | 0·082 | | | |
| H | | | 473 | 0·301 | 0·445 |
| | 493 | 0·786 | 483 | 0·041 | |
| | | | 509 | 0·103 | |
| | 352 | 0·262 | 393 | 0·001 | |
| | 309 | 0·270 | 322 | 0·011 | |
| | 300 | 0·015 | | | |
| | 282 | 0·114 | 278 | 0·501 | |

[a] Calculated according to refs 17 and 19.

pointed out, theoretical *f* values are about twice the experimental value, which is in good accord with our data (Table 4) for the long wavelength transitions determining the color of both tautomeric structures.

A quantitative investigation of the substituted 1-phenylazo-2-naphthols and isomeric 2-phenylazo-1-naphthols is in progress and the results obtained will be reported later.

## ACKNOWLEDGEMENT

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