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Azo-Quinonehydrazone Tautomerism in 2-Phenylazo-1-Naphthol

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ABSTRACT

The tautomeric equilibrium of 2-phenylazo-1-naphthol in 13 different solvents is analysed using a previously developed quantitative approach. The spectral characteristics of both tautomeric forms and the tautomeric constants K_T are determined and compared with those of the isomers 1-phenylazo-4-naphthol and 1-phenylazo-2-naphthol. The long wavelength band at about 500 nm, determining the colour, corresponds to the hydrazone form and consists of three vibrational sub-bands. The low sensitivity towards changes in solvent polarity and the highest content of hydrazone form within the three isomeric phenylazonaphthols explains the wide use of dyes containing a 2-phenylazo-1-naphthol moiety. PPP-MO calculations were in good agreement with the experimental spectral data for both tautomeric forms. The redistribution of the π-electronic density during the $S_0 \rightarrow S_1$ *transition is calculated for both tautomeric forms, and its influence on substituent effects, dye–solvent interaction and colour strength is discussed.*

INTRODUCTION

2-Phenylazo-1-naphthol (**I**) and its derivatives (Fig. 1) are widely used dyes and represent about 26% of the commercially disclosed structures of azo dyes.[1] Spectral and quantum chemical investigations, i.e. their colour prediction, are therefore of theoretical and technological value.

The dyes **I** can exist in two possible tautomeric structures, azo ($\mathbf{I_A}$)

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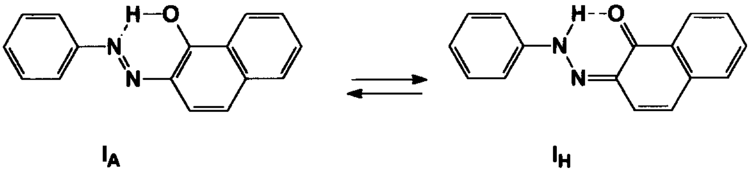


Fig. 1. Azo-quinonehydrazone tautomerism of 2-phenylazo-1-naphthol.

and hydrazone (I_H), stabilized to a significant extent by intramolecular H-bonding.[2] It has been shown that **I** exists predominantly[3,4] or exclusively[5,6] in its hydrazone from I_H. This conclusion is drawn from the lack of a distinct band in the 380–420 nm region of the absorption spectrum (a region within which the long wavelength absorption band for the **A**-form is observed), together with results of NMR studies in deuterated chloroform.

The existence of a strong intramolecular H-bond is the main cause of the weak mobility of the tautomeric equilibrium $I_A \rightleftharpoons I_H$ towards environmental factors such as solvent polarity changes. The spectral changes observed are much less pronounced than in the isomeric 1-phenylazo-4-naphthol (**II**) and 1-phenylazo-2-naphthol (**III**)[7,8] and limit the application of existing approaches for quantitative spectral analysis. The quantitative evaluation of the tautomeric equilibrium in **I** is difficult and only earlier qualitative conclusions are available.[3-5]

The introduction of computer methods for spectral data processing, based on the resolution of complex absorption bands,[9,10] and the use of integral intensities instead of absorption values in some particular cases in quantitative analysis,[11] assists in the analysis of complicated equilibria where the spectral changes are small. Using these approaches, the tautomeric equilibria in **II**[12] and **III**[8] have been successfully investigated.

The aim of this study is to analyse quantitatively the tautomeric equilibrium $I_A \rightleftharpoons I_H$ in different solvents, to estimate their influence and to compare the spectral characteristics of the azo and hydrazone tautomeric forms with the π-electronic transitions derived from the PPP-MO approach.

MATERIALS AND METHODS

2-Phenylazo-1-naphthol was obtained as a by-product in the coupling reaction of diazotised aniline with 1-naphthol. The two isomeric phenylazonaphthols **I** and **II** were separated by column chromatography. The purity of compound **I**, m.p. 134–135°C, was checked by TLC and its spectral characteristics were in accord with published data.[3-5]

The absorption spectra of **I** were obtained on a Lambda 17 UV-Vis spectrophotometer (Perkin Elmer). Isomolar solutions in 13 different solvents were measured at constant temperature (25°C) and analysed with the original programmes for the resolution of overlapping bands and quantitative analysis of tautomeric equilibria, as described elsewhere.[9–11] The quantum chemical calculations were carried out using a conventional PPP SCF-CI program, suitable for use on a personal computer. The parameters suitable for the potentially tautomeric phenylazonaphthols, including $\mathbf{I}_A \rightleftharpoons \mathbf{I}_H$, are those given by Griffiths *et al.*[13–15]

RESULTS AND DISCUSSION

The absorption spectra of **I** in three different solvents are presented in Fig. 2. The observed spectral changes are rather small, even in comparison with those in **III**.[8] There is no visual evidence for a band around 380–420 nm, which could be assigned to the azo form $\mathbf{I}_A$. However, this is not sufficient evidence to conclude that no azo tautomer exists, since in the corresponding second derivative spectral curves (Fig. 3) a band at about 420 nm is clearly visible. The second derivative band at about 340 nm could possibly also be associated with an azo band.

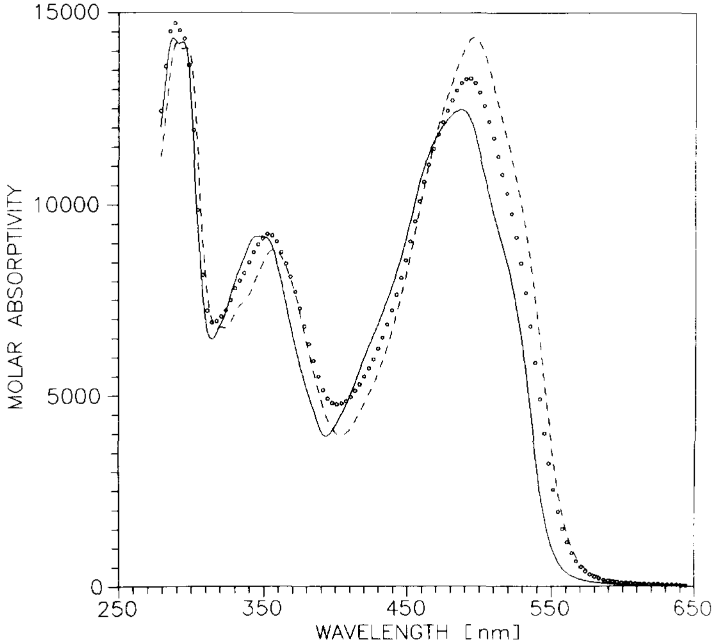


Fig. 2. Absorption spectra of **I** in dichloromethane (– – – –), methanol (oooooo) and *i*-octane (———).

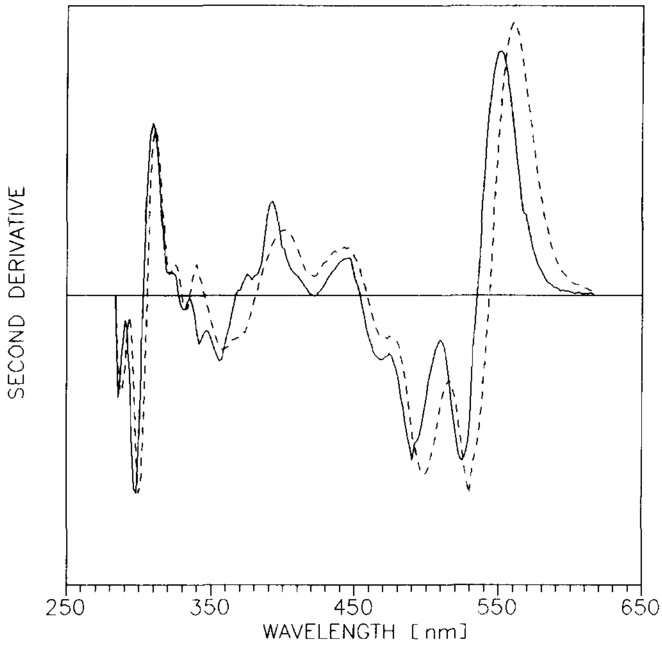


Fig. 3. Second derivative spectra $d^2A/d\nu^2$ of **I** in dichloromethane (– – – –) and *i*-octane (———).

Although the spectral changes are small, the absorption spectra in the 13 solvents were analysed using a quantitative approach developed and applied earlier.[8,11,12] The absorption spectrum of **I** in *i*-octane, together with the resolved individual bands assigned to both tautomeric forms, is presented in Fig. 4. The long wavelength band at about 500 nm corresponds to the $\mathbf{I}_H$ form and consists of three sub-bands, which most probably are vibrational in nature. This finding is strongly supported by the second derivative spectra (Fig. 3), as well as by the previous studies of Gabor *et al.*,[3] who showed that at −182°C in methylcyclohexane : *i*-hexane (1 : 1) a distinct vibrational structure consisting of three sub-bands of the long wavelength hydrazone band is observed.

The spectral characteristics for both tautomeric forms, together with the molar parts of the A-form (X_A), and the tautomeric constants K_T = [H]/[A] in the 13 solvents, are presented in Table 1. Most probably the small changes observed in the X_A and K_T values on changing the solvent polarity are due to the strong intramolecular H-bond imparting relative stability to the tautomeric equilibrium $\mathbf{I}_A \rightleftharpoons \mathbf{I}_H$ towards external influences. Although the observed changes are within 10% (which does not allow a clear unidirectional interpretation to be made), it should be noted that the direction of these changes is very similar to that observed in their

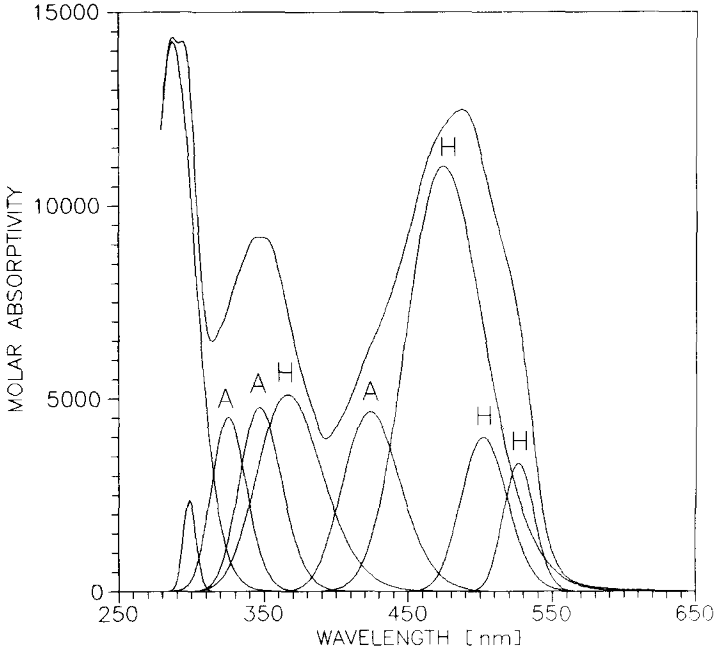


Fig. 4. Absorption spectrum of **I** in *i*-octane, with resolved individual bands.

structural analogues **II** and **III**[8,11,12] where the changes are much more pronounced and allow their classification.

The relation between the molar absorptivities of $\mathbf{I}_A$ and $\mathbf{I}_H$ in their maxima (Table 1) also differs and again, as in the case of the structural isomers **II** and **III**,[8,11,12] the **H**-form has the more intense absorption in the visible region, i.e. higher colour strength, a fact which is especially important for coloristic and technological properties.

The spectral characteristics of the **A**- and **H**-forms in **I-III**, and also the calculated X_H and K_H values in *i*-octane and ethanol, are shown in Table 2. Comparison shows that the content of the **H**-form increases in the order **II** < **III** < **I** in accordance with the observations of Lyčka *et al.*[16] based on ^{13}C NMR. The low sensitivity towards changes in solvent polarity and the highest content of the **H**-form could explain the established fact[1] that the azo dyes of type **I** are the most widely used.

The calculated individual spectra of both tautomeric forms $\mathbf{I}_A \rightleftharpoons \mathbf{I}_H$ in selected solvents are presented in Fig. 5. It is interesting to compare the spectral characteristics of $\mathbf{I}_A$ and $\mathbf{I}_H$ with the corresponding π-electronic transitions using the PPP-MO method. The calculated transition energies and oscillator strengths f^{calc}, and the experimentally obtained values of λ_{max} and f^{exp} for both tautomeric forms $\mathbf{I}_A$ and $\mathbf{I}_H$ are shown in Table 3. A good agreement between the values is observed, although to some extent

TABLE 1
Calculated Values of X_A and K_T and Spectral Characteristics of Both Tautomeric Forms in the Investigated Solvents

Solvent	*Origin, Purity*	D^a	X_A (%)	K_T	*A-form*		*H-form*	
					λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}
Dichloromethane	Merck, spectral	8·93	28·2 ± 0·4	2·54	424·8	12 100	496·8	19 920
Chloroform	Fluka, p.a.	4·81	28·3 ± 0·4	2·53	426·4	11 470	498·4	20 130
1,2-Dichloroethane	Merck, extra pure	2·18	30·3 ± 0·4	2·30	424·8	11 880	496·8	19 990
Acetonitrile	Fluka, spectral	37·50	31·0 ± 0·4	2·22	423·2	12 100	492·0	19 770
Carbon tetrachloride	Merck, pure	2·24	31·9 ± 0·4	2·13	424·8	12 180	493·6	19 890
Ethanol	Fluka, 96% spectral	24·55	32·1 ± 0·4	2·11	423·2	11 370	495·2	19 720
Methanol	Merck, spectral	32·70	32·7 ± 0·3	2·05	421·6	11 690	492·0	19 650
Ethyl acetate	Fluka, p.a.	6·02	35·4 ± 0·3	1·82	421·6	12 080	492·0	20 270
Acetone	Merck, spectral	20·70	35·8 ± 0·5	1·79	423·2	12 670	492·0	19 870
Dimethyl sulfoxide	Merck, spectral	46·68	37·7 ± 0·4	1·65	416·8	12 250	498·4	18 170
Cyclohexane	Fluka, spectral	2·02	38·3 ± 0·4	1·61	424·8	11 870	488·8	20 440
Dimethyl formamide	Merck, spectral	36·71	38·4 ± 0·3	1·60	416·8	11 640	496·8	19 200
i-Octane	Riedel-de Haen, spectral	1·94	39·9 ± 0·4	1·50	423·2	11 670	487·2	20 550

[a] Dielectric constant, Fluka 1993/1994, p. 1526.

the calculations overestimate the colour strength of the hydrazone structure I_H. In this respect, the very pronounced temperature dependence of the absorption intensity in the visible region observed by Gabor *et al.*[3] must be noted.

The redistribution of the π-electron density during the $S_0 \rightarrow S_1$ electronic transition determines the influence of factors such as substituent effects, dye–solvent interactions and the intensity of this transition. The change of the π-electronic density during the $S_0 \rightarrow S_1$ transition could be illustrated schematically, showing the contribution of each atom in the charge transfer proceeding in both tautomeric structures (**A** and **H**). The

TABLE 2

Spectral Characteristics Calculated for the Pure Tautomeric Forms of **I-III**

Compound	*Solvent*	X_H (%)	K_T	*A-form*		*H-form*	
				λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}
I	ethanol	67·9	2·11	423·2	11 370	495·2	19 720
	i-octane	60·1	1·50	423·2	11 670	487·2	20 550
II	ethanol	19·4	0·24	407·2	15 560	479·2	34 430
	i-octane[a]	10·4	0·11	385·0	16 600	476·0	27 200
III	ethanol	42·0	0·72	413·6	16 970	482·4	34 190
	i-octane	33·1	0·49	413·6	16 200	480·8	32 910

[a] According to Ref. 7.

differences between the calculated π-electron densities, $\Delta Q_i = Q_i^{S_1} - Q_i^{S_0}$, for each atom *i* of both tautomeric structures are shown in Fig. 6, where the overall area of the circles is proportional to ΔQ_i. The shaded circles correspond to an increase, and empty ones to a decrease, in π-electron density upon excitation of the molecule.

The transition moment directions of the first electronic transitions for

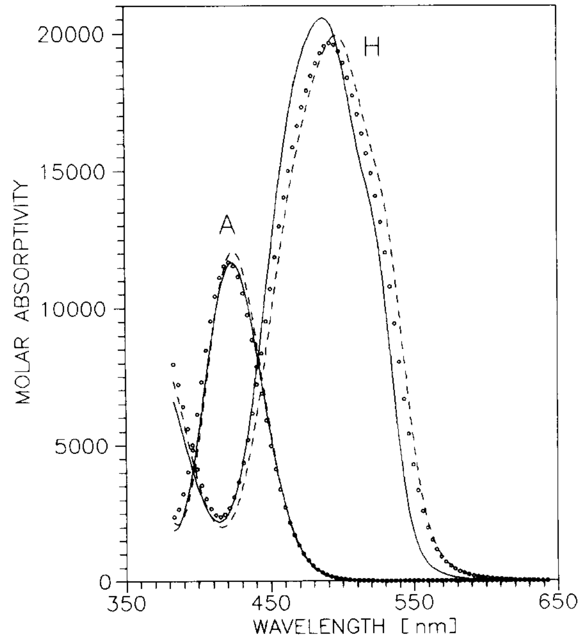


Fig. 5. Individual absorption curves of both tautomeric forms of **I** in dichloromethane (– – – –), methanol (oooooooo) and *i*-octane (———).

TABLE 3
Comparison Between the Calculated (PPP-MO) Electronic Transitions and the Individual Spectral Bands of Both Tautomeric Forms of **I** in *i*-Octane and their *f* Values

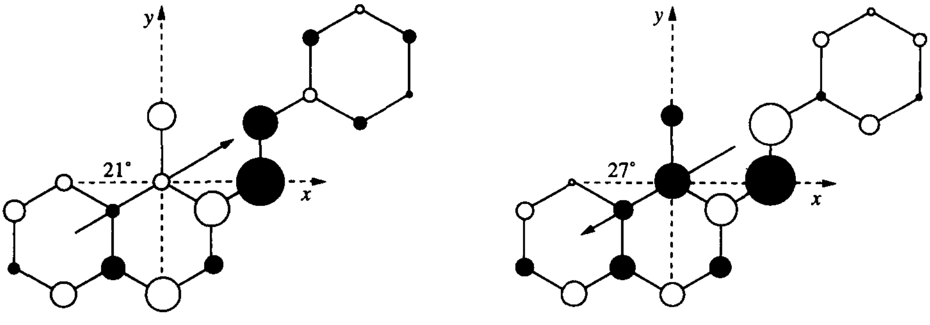
Form	λ_{max}^{calc} *(nm)*	f^{calc}	$\lambda_{max}^{exp\ a}$ *(nm)*	$\lambda_{max}^{obs\ b}$ *(nm)*	$f^{exp\ a}$	$f^{obs\ b}$
A	429	0·681	423	423	0·139	0·139
	323	0·187	347	335	0·155	0·292
	300	0·654	325		0·137	
H			526		0·022	
	498	0·993	505	487	0·044	0·305
			474		0·239	
	334	0·113				
	315	0·126	366	366	0·153	0·153
	301	0·013				

[a] Estimated from Fig. 4 according to Refs 9 and 10.

[b] From the individual spectral curves of I_A and I_H (Fig. 5).

both tautomeric structures are also given in Fig. 6. It should be noted that in the azo dyes **I-III**, in all cases the charge transfer of the azo structure proceeds mainly from specific sites in the naphthol ring towards the azo group and to a smaller extent to the phenyl ring. The opposite is true for the hydrazone structure—the charge transfer proceeds mainly from the phenyl ring and aniline-like N-atom towards specific sites in the naphthoquinone ring and the quinoneimine N-atom. These findings reflect another important colour related property—the calculated transition moments are in opposite directions for both tautomeric structures.

Such a treatment of spectral data and PPP-MO calculations explains the experimental observations, and enables important colouristic properties of dyes with specific tautomeric structure to be evaluated.



Azo Quinonehydrazone

Fig. 6. Schematic presentation of ΔQ_i for the two tautomeric **A** and **H** forms.

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