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AZO–HYDRAZONE TAUTOMERISM OF HYDROXYAZO COMPOUNDS—A REVIEW

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SUMMARY

The phenomenon of azo–hydrazone tautomerism of hydroxyazo compounds is reviewed in relation to structural factors such as the degree of annellation and the type and position of substituents, as well as environmental factors which are determined by the medium containing the tautomeric entity. Media effects are discussed with reference to studies in solution, polymeric substrates, the crystalline solid state and the gas phase. The influence of the state of the tautomeric equilibrium on the chemical reactivity is considered with an emphasis on the practically important aspects of photochemistry and acid–base behaviour of tautomeric hydroxyazo dyestuffs.

1. INTRODUCTION

Following the discovery in 1870 of the now well-known coupling reaction between diazonium salts and phenols,[1] the coloured products were believed to be hydroxyazo compounds. The first challenge to this view was made in 1883 by Liebermann[2] who postulated that the hydroxyl proton of 1-phenylazo-2-naphthol, **II**(R = H), was labile and could be capable of bonding with a nitrogen atom of the azo group. Evidence to support Liebermann's assertion came the following year when Zincke and Bindewald[3] reported that they obtained the same product either by coupling the benzene diazonium ion with 1-naphthol or by condensing phenylhydrazine with 1,4-naphthoquinone. The exact nature of this product led to much heated debate since there was clear chemical evidence for both hydroxyl and carbonyl functionality (e.g. refs. 4–6). Eventually Kuhn and Bär[7] proved the

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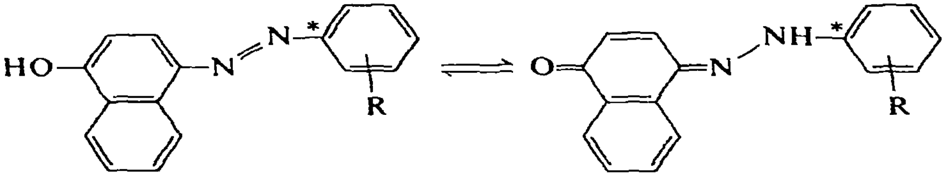
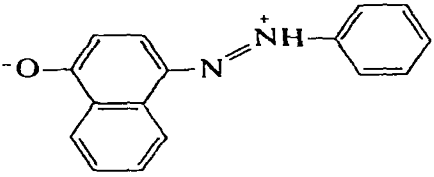


I 4-Phenylazo-1-naphthol

existence of a rapidly formed tautomeric equilibrium of the type **I**(R = H) between the azo and hydrazone forms. It is now known that this equilibrium is influenced by both structural factors within the molecule and by the nature of the medium surrounding the molecule.

The possibility of a zwitterionic structure **IA** for **I**(R = H) was suggested by Millefiori *et al.*[8] to account for the high experimental values of its dipole moment.



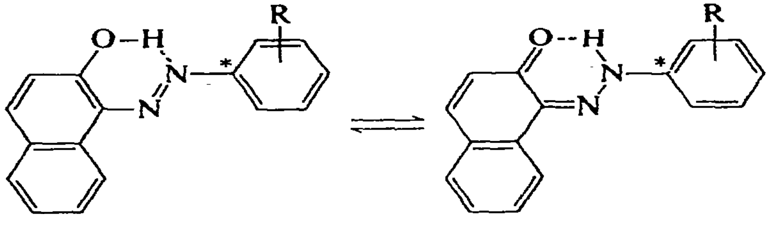
IA

Infrared spectra of **I**(R = H) and **II**(R = H) have also suggested zwitterionic structures.[9] However, Goursot *et al.*[10] concluded from molecular orbital calculations, supported by experimental evidence, that such a species did not exist.

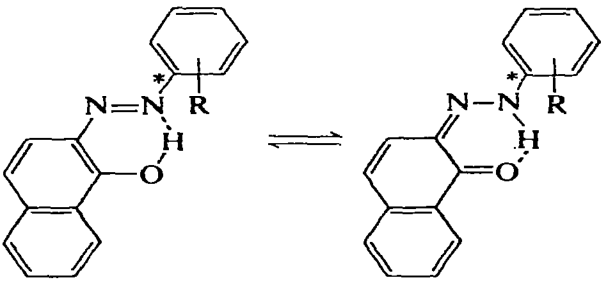
The phenomenon of azo–hydrazone tautomerism has been the subject of much research and is well documented in the literature. Several reviews dealing with work up to 1972 have been published.[6,9,11] This report essentially covers the period 1970–1980.

2. STRUCTURAL FACTORS

The state of the tautomeric equilibrium for *ortho* and *para* hydroxyazo compounds is primarily determined by structural factors within the molecule. Millefiori *et al.*[12] reported that certain derivatives of **II** were essentially azo compounds, but a number of studies[9,13–17] have indicated that the presence of a strong intramolecular H-bond in the *ortho* derivatives, e.g. **II** and **III**, has the effect of favouring the hydrazone tautomer and of stabilizing the equilibrium against external influences such as a change of solvent. No such stabilization is possible in the case of the *para* derivatives, e.g. **I**, and this tends to render the equilibrium of these compounds much more susceptible to the influence of environmental factors.[14,16,17]



II 1-Phenylazo-2-naphthol

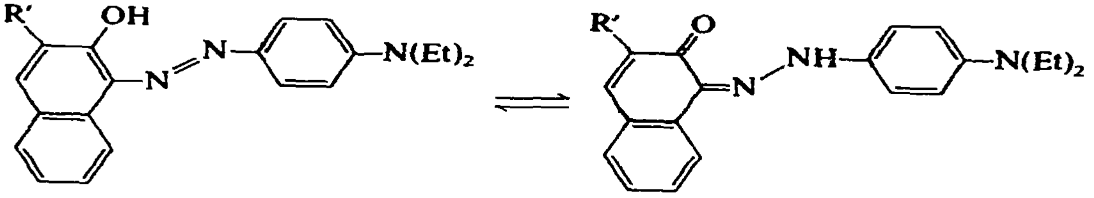


III 2-Phenylazo-1-naphthol

The position and nature (electron withdrawing or releasing) of substituents can also have a bearing on the state of the tautomeric equilibrium. Both experimental results (e.g. ref. 13) and theoretical considerations[18] have indicated that there is a general tendency for electron withdrawing groups R (see **I**, **II**, **III**) to stabilize the hydrazone tautomer. An early explanation by Burawoy *et al.*[13] attributed this to the fact that the C*—NH bond (see **I**, **II**, **III**) of the hydrazone form is more polarizable than the C*—NN bond of the azo tautomer. Thus an electron deficiency at C* (caused by an electron withdrawing substituent R) would favour the adoption of the hydrazone form. More recently, Kishimoto *et al.*[19] pointed out that the azo group (—N=N—) is an electron acceptor whereas the imino group (—NH—) is an electron donor. Thus an electron donating substituent R (see **I**, **II**, **III**) stabilizes the azo tautomer and the hydrazone tautomer is favoured if R is an electron withdrawer.

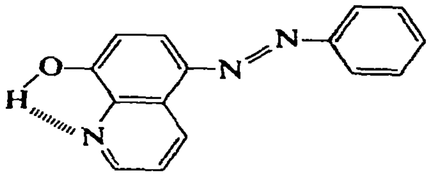
However, in the case of **I**, R = *ortho* substituent, the hydrazone form is present in lower concentrations than expected. This discrepancy has been explained by steric hindrance which prevents the —NH— group of the hydrazone tautomer from participating in H-bonding with suitable solvents. Instead, the —OH group of the azo form becomes H-bonded to the solvent.[14]

Normally, derivatives of **II** in which R is a strong electron releasing group in the *para* position exist mainly as azo compounds,[20,21] but deviations from this general observation have been documented. For example, Kostyuchenko *et al.*[21] examined a number of azo dyes of general structure **IV** and found that certain substituents such as —OH, —COOH, —$CONH_2$, —$CONHC_6H_4OCH_3$ (R′ in **IV**) stabilized the hydrazone tautomer by intramolecular H-bonding to the carbonyl group.

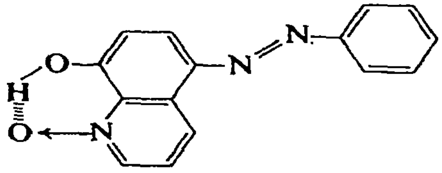


IV

Intramolecular H-bonding is also responsible for the stabilization of the azo forms of **V** and **VI**.[9]

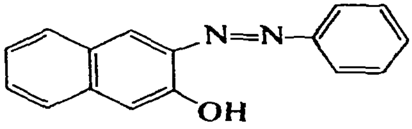


V

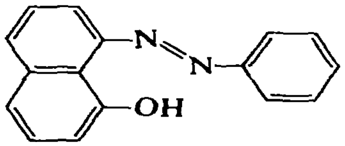


VI

Compounds such as **VII** and **VIII** are true azo compounds, probably as a consequence of the fact that a hydrazone structure cannot form without completely removing the aromatic character of the naphthalene system.[11]

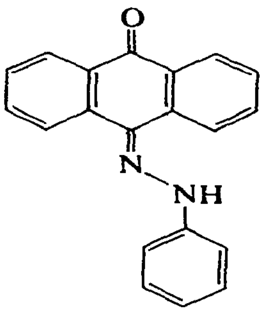


VII



VIII

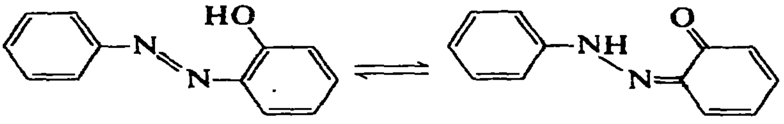
Theoretical considerations have shown that the hydrazone form of a tautomeric system becomes progressively more stable as the size of the ring system bearing the O atom increases.[18] Thus it is found experimentally that phenylazoanthrols, e.g. **IX**,



IX

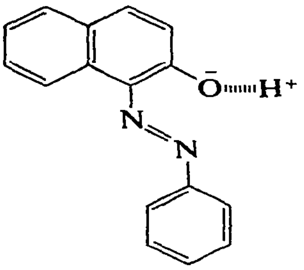
exist solely as hydrazones.[9,11,21] Although some workers[6,9,11,22–24] have maintained that phenylazophenols are true azo compounds and cannot be observed as hydrazones, it is now widely accepted that these compounds are subject to the same substituent effects as described for phenylazonaphthols, although they are less susceptible to these effects.[25,26]

A theoretical analysis of the structure of *o*-hydroxyazobenzene, **X**, has acknowledged the likelihood of the tautomeric equilibrium **X**$\rightleftharpoons$**XI**.[27]



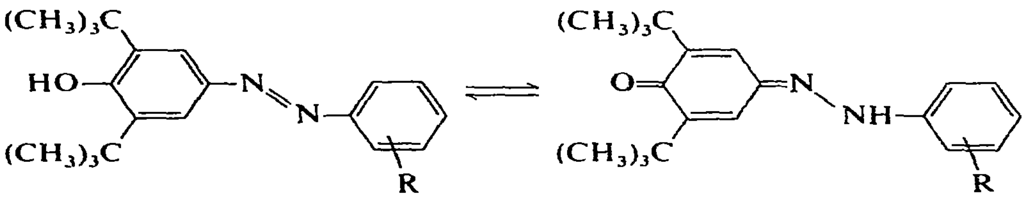
X **XI**

In addition, Rau[28] detected weak fluorescence in solutions of *o*- and *p*-hydroxyazobenzene which indicated that small concentrations of the hydrazone tautomer were present. (It has been demonstrated that the azo tautomers are non-fluorescent in most cases,[29] and emission is due solely to the hydrazone forms,[28,30,31] although Nurmukhametov *et al.*[32] claimed that a bipolar ion (e.g. **XII**) was responsible for fluorescence.)



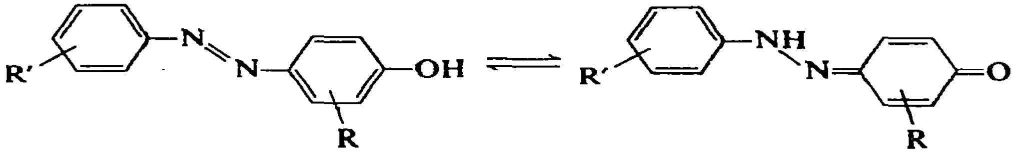
XII

For some time it has been accepted that certain sterically hindered azophenol compounds of general structure **XIII** show a tendency to adopt a quinoid hydrazone form **XIV**, which is enhanced by electron withdrawing substituents R.[9,11] However, Hofer and Huffmann[25] did not find steric hindrance to be a necessary criterion for



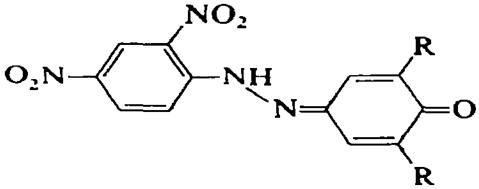
XIII **XIV**

hydrazone formation. They reported that the equilibrium **XV**$\rightleftharpoons$**XVI** was influenced by an electron 'push–pull' due to substituents. The hydrazone form **XVI** was stabilized by R′ being an electron withdrawer and R an electron releaser, whereas reversing this situation favoured the azo tautomer **XV**.[25]



XV **XVI**

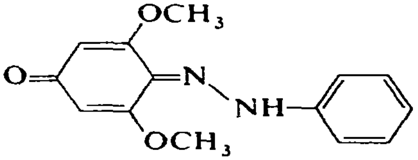
Subsequently, Juwick and Sundby[26] found that the equilibrium of 4-(2′,4′-dinitrophenylazo)alkylphenols could be influenced so as to favour predominantly the hydrazone tautomer, e.g. **XVII**. This was accomplished by ensuring the presence of one or two alkyl groups *ortho* to the hydroxyl group. Chelate bonding of the —NH— proton with the 2′-NO_2 group is likely.[25]



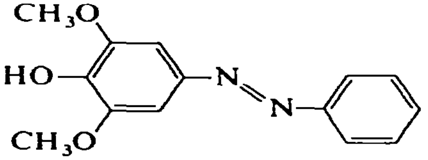
(R = alkyl)

XVII

An interesting result was obtained by Jacques *et al.*[33] who observed symmetrical dimethoxy derivatives of 4-hydroxyazobenzene using UV, ^{1}H and ^{13}C NMR techniques. Compound **XVIII** was found to be exclusively hydrazone while **XIX** existed as an azo compound.



XVIII



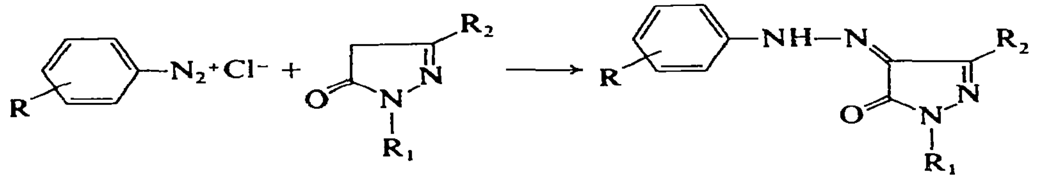
XIX

A number of theoretical studies concerned with conformational analysis of tautomeric systems have been published. The Hückel molecular orbital (HMO) method was used by Gribov *et al.*[34] to calculate the ratios of absorption band maxima for the tautomers of three hydroxyphenylazo naphthols (**I**, **II**, **III** with R = *o*-OH in each case). Agreement between the theoretical calculations and experimental spectra for I(R = *o*-OH) was obtained only after a non-planar model was used. Subsequently, Jacques *et al.*[35] applied the Perturbative Configuration Interaction using Localized Orbitals molecular orbital (PCILO MO) method and showed that a number of distinctly non-planar conformers of II(R = H) were possible. These workers also used the PCILO MO method to determine the theoretically optimum structures of conformers of 4-hydroxyazobenzene, 1-phenylazonaphthalene, and both tautomers of 4-phenylazo-1-naphthol (I, R = H).[10]

Chernova *et al.*[36] have discussed the UV spectra of tautomers of **I** and **II** (R = *p*-SO_3H in each case) with regard to the theoretical results determined by MO calculations, and an earlier report has discussed the electronic transitions of a large number of hydroxyazo compounds in the UV and visible regions.[37] In the latter report, MO calculations agreed with experimental spectra, and for I(R = H) the absorption band of the azo tautomer in the visible region was found to coincide with the calculated first $\pi \rightarrow \pi^*$ electronic transition.

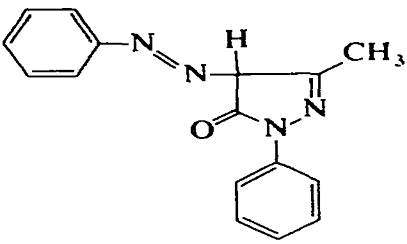
2.1. *Other tautomeric systems*

Pyrazolone dyes are potentially tautomeric entities and Parent[38] has reviewed attempts to characterize their molecular structure. It has now been shown[39,40] that the true structure of the coupling product of **XX** and **XXI** is compound **XXII** (see Scheme 1), although a previous NMR study[41] reported that compound **XXII** ($R = H$, $R_1 = C_6H_5$, $R_2 = CH_3$) had the structure **XXIIA** while in solution in $CDCl_3$, CCl_4 or CH_2Cl_2 between 0 and −60 °C. Theoretical studies have also dealt with the structure and tautomerism of arylazoprazolones.[42,43]



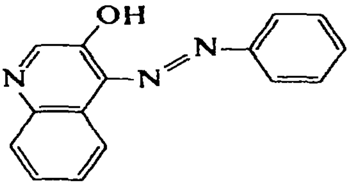
XX **XXI** **XXII**

Scheme 1

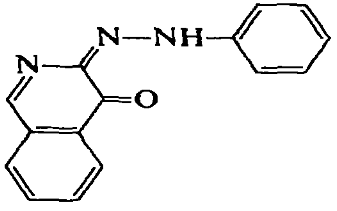


XXIIA

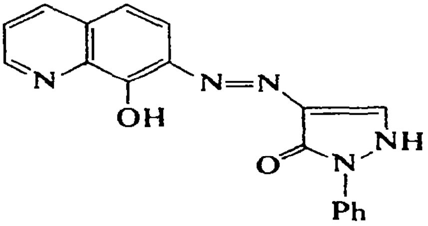
The incidence of a tautomeric equilibrium for hydroxyquinoline derivatives has been confirmed by theoretical and experimental studies. Molecular orbital calculations have indicated that the azo structure **XXIII** of 3-hydroxy-4-(phenylazo) quinoline is more stable than its hydrazone tautomer, but that the hydrazone structure **XXIV** of 4-hydroxy-3-(phenylazo)isoquinoline is more stable than its azo tautomer.[44] Infrared and electronic spectral data later confirmed these predictions and further showed that electron withdrawing substituents in the *para* position of the phenyl ring of **XXIII** shift the equilibrium in favour of the hydrazone tautomer.[45] Russian workers have shown that the most stable form of 7-(4-antipyrylazo)-8-hydroxyquinoline in neutral solution has azo functionality, **XXV**.[46]



XXIII

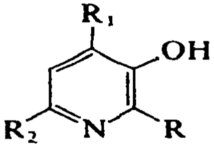


XXIV



XXV

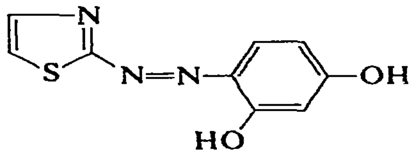
Ultraviolet spectral data have demonstrated the occurrence of a tautomeric equilibrium in a number of substituted 3-pyridinols, **XXVI**.[47] The tendency for **XXVI** to adopt a hydrazone structure was reduced in the case of the corresponding *N*-oxides.[47]



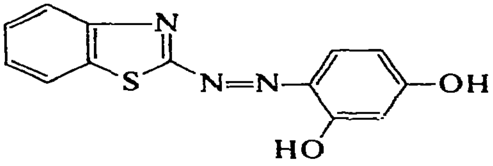
$R, R_1, R_2 = H—, Me—, R_3Ph—, R_4PhN_2—$

XXVI

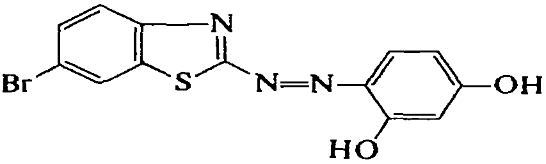
Olenvich *et al.*[48] recently reported using MO calculations, supported by IR spectral data, to show that **XXVII**, **XXVIII** and **XXIX** exist in tautomeric equilibrium. A similar equilibrium was found to apply to the corresponding 1-substituted-2-naphthols and 6-substituted-3-$Et_2NC_6H_4OH$ analogues.[48]



XXVII

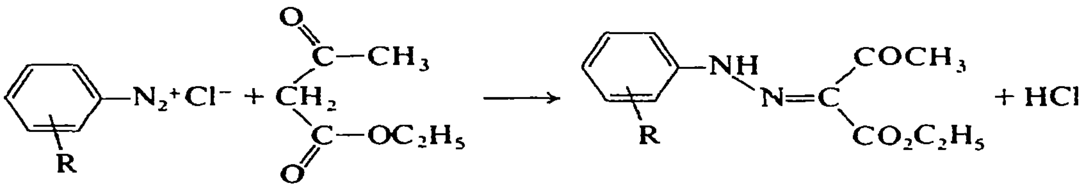


XXVIII



XXIX

Phenyl diazonium salts are capable of coupling with aliphatic compounds to yield tautomeric moieties. The hydrazone tautomer is believed to be the stable product of coupling an aromatic diazonium compound with a methylene group of a ketone[49] or a β-diketone[50,51] and also of keto-esters such as ethyl acetoacetate[52] (see Scheme 2).



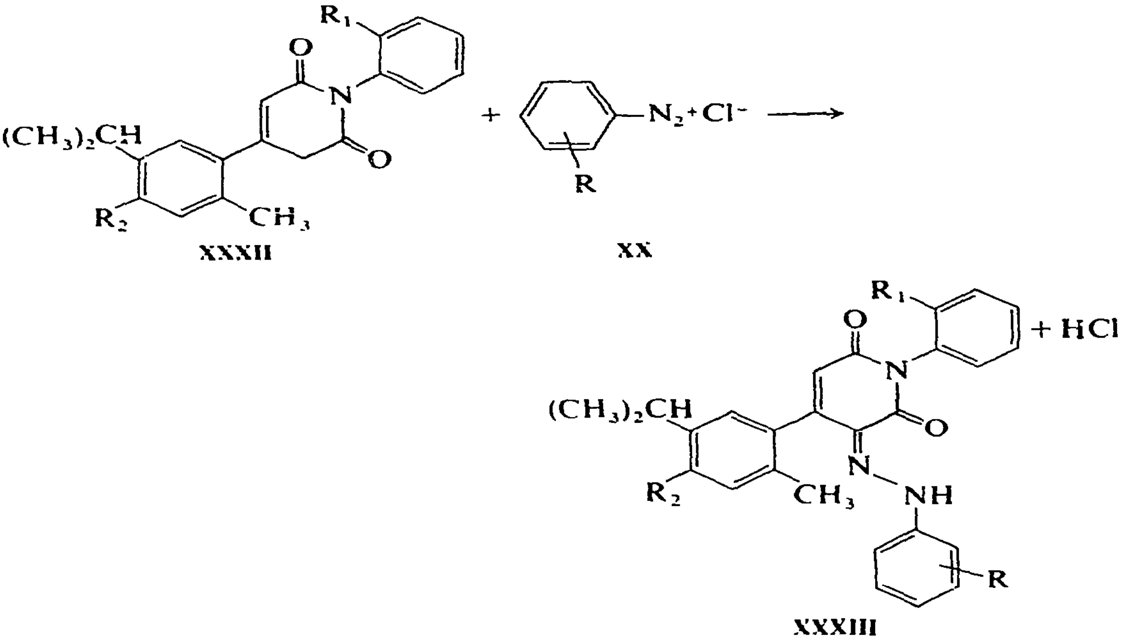
XX XXX XXXI (*cis* and *trans*)

Scheme 2[52]

Experimental evidence in the form of IR spectral[49] and NMR[52] data, as well as a polarographic study,[51] have confirmed this proposal.

The reaction of benzenediazonium chlorides with certain aromatic dicarbonyls has also yielded products with hydrazone functionality, e.g. Scheme 3.[53]

In addition, the condensation product of phenylhydrazine and 1,2,3-tricarbonyl compounds is believed to exist preferentially in the hydrazone form.[54,55]

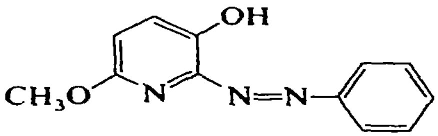


XXXII XX XXXIII

Scheme 3

3. ENVIRONMENTAL FACTORS

Although structural factors play a significant role in determining the tautomeric equilibrium, the medium containing the molecules can also exert a strong influence. Thus changing the environment of a tautomeric system can often cause dramatic changes in equilibrium. For example, the equilibrium of **XXXIV** has been shown to be placed in favour of the hydrazone tautomer by aggregation, by increasing solution acidity and by more nucleophilic solvents.[56,57] In the gas phase, where environmental factors are essentially eliminated, the equilibrium of **XXXIV** appears to fully favour the azo tautomer.[57] It should be noted that studies of azo-hydrazone tautomerism in solution can be complicated by aggregation[11,58] and it has been suggested that the hydrazone tautomer is more susceptible to aggregation than the azo tautomer.[59]



XXXIV

3.1. *The effect of solvents*

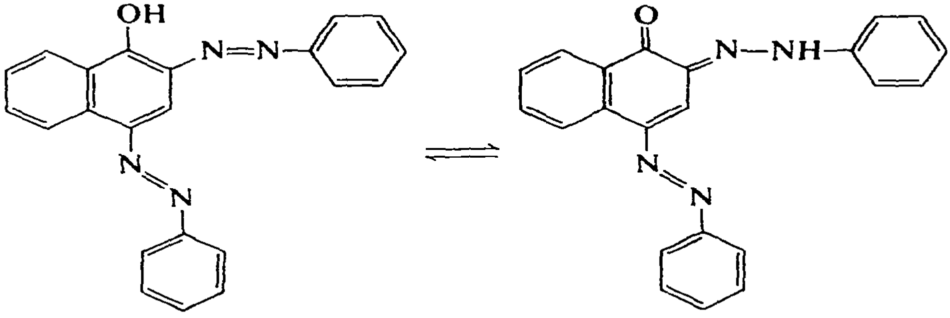
The role of the solvent in determining the extent of the tautomeric equilibrium can be quite significant. For example. Korewa and Urbanska have reported[60] that I(R = *o*-Cl) was present as 100 % azo compound in acetone but as 100 % hydrazone in benzene. Contrasting with this, they found I(R = *o,p*-dichloro) to be solely in the azo form in both acetone and benzene, which indicates the overriding nature of the substituent effect in this case. The state of the tautomeric equilibrium for a total of 14 derivatives of **I** in a variety of solvents has been described by Korewa and Urbanska[60] and reproduced elsewhere.[11]

Specific polar or H-bonding interactions are believed to be important determinants of the state of the tautomeric equilibrium, but the exact way in which these interactions operate is often obscure. After applying the Hückel MO method to the problem, Kuder[18] generalized that the formation of inter- and intramolecular H-bonds stabilizes the hydrazone tautomer of hydroxyarylazo compounds. Experimentally it is found that increasingly polar solvents (non-H-bonding) tend to favour the more polar hydrazone form of *ortho* and *para* hydroxyazo compounds.[61] However, in the case of the *para* derivatives (**I**) a complication arises because the formation of H-bonds with suitable solvents stabilizes the azo form, since the —OH group of the azo tautomer is able to form a stronger H-bond than the —NH group of the hydrazone.[14]

The prototropic properties of the solvent are known to influence the position of equilibrium[60] and Hempel *et al.*[62] reported that certain protic solvents (e.g. ethanol) tended to favour the hydrazone form of I(R = *para* substituent). On the other hand, Kishimoto *et al.*[19] found that the tautomeric equilibrium of derivatives of I(R = *para* substituent) was displaced towards the azo form in pyridine, acetone, ethanol and methanol, but towards the hydrazone in chloroform and acetic acid. The displacement was based on the equilibrium in benzene as standard.

Reeves *et al.*[63] have suggested that the effect of cavity formation energy on the tautomeric equilibrium may dominate the effect of the establishment of specific polar interactions between the tautomeric compound and solvent. By way of example, they postulated that the hydrazone tautomer of **XXXVII** is able to reside in a solvation cavity in water which has a lower free energy than the cavity required for the azo tautomer.[63] Previously Reeves and Kaiser had been unable to correlate bulk solvent properties, such as dielectric constant, with the position of equilibrium of a series of 4′-substituted 2- and 4-arylazo-1-naphthol sulphonates.[64] They found that in neat solvents, the equilibrium depended on the solvent structure. For neat solvents capable of forming a three dimensional structure, e.g. water or formamide, the hydrazone form was favoured. In two dimensional or unstructured solvents, e.g. simple alkyl alcohols or *N*-methylformamide, the azo tautomer predominated. In binary aqueous–organic solvent mixtures the microscopic environment of the dye in the solvent matrix was the determining factor. The authors suggested that when added to an aqueous solution of the dye, the organic co-solvent selectively solvates the hydrophobic portion of the dye molecule and the state of the equilibrium is thus influenced by this 'microenvironment' around the molecule. Misuishi *et al.* arrived at the same conclusions after studying the tautomerism of I(R = H) in organic solvents containing water.[65]

Thermal influences on the tautomeric equilibrium were described by Saeva,[17] who used NMR to examine compounds **I** and **II** (R = *p*-OCH_3 in each case) in solution in acetone-d_6. Raising the temperature from −21 to 20 °C for I(R = *p*-OCH_3) and from 20 to 40 °C for II(R = *p*-OCH_3) shifted the equilibrium towards the azo tautomer in each case. Saeva[17] calculated thermodynamic parameters at 20 °C and stated that in each system the enthalpy component of the free energy favoured the hydrazone tautomer but the entropy term favoured the less polar azo form. Thus the difference in tautomeric behaviour between systems **I** and **II** (R = *p*-OCH_3 in each case) can be ascribed to the dominance of the entropy and enthalpy terms for compounds **I** and **II** (R = *p*-OCH_3 in each case) respectively. Bekarek *et al.*[41] had previously reported that the disubstituted naphthol derivative **XXXV** in solution in methylene chloride was in a tautomeric equilibrium over the temperature range −75 to 31·5 °C, but that only the hydrazone tautomer was present below −80 °C.

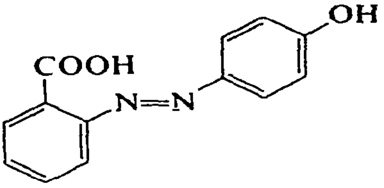


XXXV

3.2. *The effect of macromolecules*

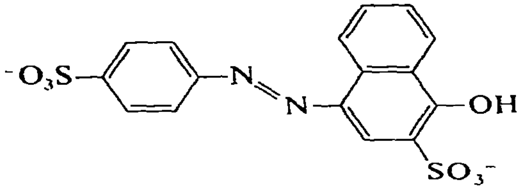
The effect of polymers on the tautomeric equilibrium of hydroxyazo compounds is of practical significance because many commercial applications of these compounds involve their incorporation in polymer substrates as colourants. However, less is known about the effects of polymers than of solvents, although the type of polymer concerned appears to be an important factor in most cases.

Several studies have dealt with the effects of polymers on tautomeric compounds in solution. For example, an aqueous solution of I(R = *p*-SO_3Na) was found by Matsui and Mochida[66] to become more acidic as increasing amounts of α- or β-cyclodextrin were added to the solution. These workers surmised that the starch formed a non-polar, aprotic microenvironment around the dye molecules which shifted the equilibrium from the less acidic hydrazone form to the more acidic azo tautomer. Previously, Korewa and Nesterowicz[67] had demonstrated that azo compounds, e.g. 4-arylazophenols, are more acidic than those containing a proportion of hydrazone tautomer, e.g. 4-arylazo-1-naphthols. However, the binding of **XXXVI** to proteins such as avidins and serum albumins in aqueous solution displaces the tautomeric equilibrium towards the hydrazone form.[68,69]



XXXVI

The equilibrium of the tautomeric dye **XXXVII** has been influenced by certain surfactants at concentrations below their CMCs.[70] As the surfactants were added to an aqueous solution of the dye, dye–surfactant aggregates formed in which surfactant was in a slight excess over dye and the tautomeric equilibrium was shifted in favour of the azo tautomer. The microenvironment of the dye within these aggregates was largely non-aqueous, in contrast to the bulk environment in the bath.

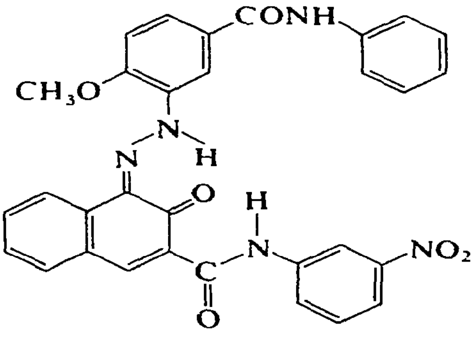


XXXVII

Diffuse reflection spectroscopy has been used to study the tautomeric equilibrium of hydroxyaryl azo dyes in crystalline NaCl[71] and on polymer substrates.[72,73] Dehari *et al.*[71] reported that both tautomers of a number of substituted 1-phenylazo-2-naphthols (**II**) were present when dry samples of the dyes were ground with NaCl. Furthermore, they demonstrated that increasing the temperature of the system shifted the equilibrium in some cases, e.g. towards the azo tautomer for **II**($R = p\text{-}NO_2$) and towards the hydrazone tautomer for **II**($R = o\text{-}NO_2$). However, decreasing the dye concentration ($1{\cdot}0 \rightarrow 0{\cdot}01$ %) favoured the hydrazone tautomer in every instance and this was related to the possibility that at lower concentrations a greater proportion of the dye is capable of being well dispersed and adsorbed on to the highly polar surface of the salt crystals. When the same dyes were applied to filter paper, tautomeric equilibrium changes were observed in certain cases after exposure to a high humidity environment.[72] The direction of the equilibrium change again depended on the position and nature of substituents. For example, the moist environment favoured the azo tautomer of **II**(R = *o*-NO_2) and the hydrazone form of **II**(R = *p*-NO_2). A later study[73] used the same dyes but employed less hygroscopic substrates than cellulosic filter paper. The substituted 1-phenylazo-2-naphthols (**II**) were deposited on such fibrous polymers as polypropylene, polyacrylonitrile, poly(ethylene terephthalate), and nylon-6,6, and their diffuse reflection spectra compared with the absorption spectra determined in solvents considered to be models of the above polymers, viz. *n*-hexane, acrylonitrile, methyl benzoate and formamide respectively. From the similarity of these spectra, the authors concluded that the 'nature' of the fibres was the major factor affecting the equilibrium, and that the effect of moisture was small in the case of the non-hygroscopic substrates.[73] Hempel and Viola[74] have also described the use of diffuse reflection spectroscopy for the determination of the tautomeric fraction of a number of hydroxyazo compounds (**I**) present in polyamide fibres and films.

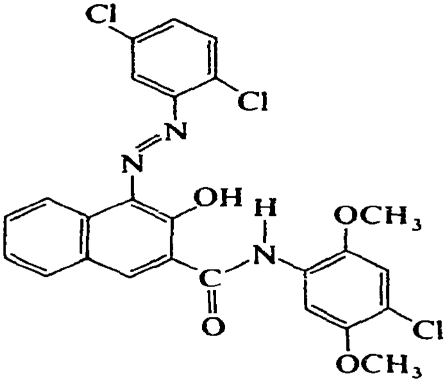
3.3. *Crystalline solid state studies*

The elucidation of the molecular structure of tautomeric entities in the solid crystalline form has received attention of late. Three dimensional diffractometry at room temperature revealed that **II**(R = *o*-NO_2, *p*-Cl) is an essentially planar molecule with hydrazone functionality.[75] In addition the magenta colourant, Pigment Red 31 (**XXXVIII**) has been characterized as having a hydrazone structure in the solid state.[76]



XXXVIII Pigment Red 31

Kobelt *et al.*[77] studied the crystal structure of Pigment Brown 1, **XXXIX**, using X-ray methods and reported that neither the hydrazone nor the azo form alone could fully account for the observed bond relationships. They added that the molecule could be regarded as being a completely conjugated planar system stabilized by intramolecular H-bonds.



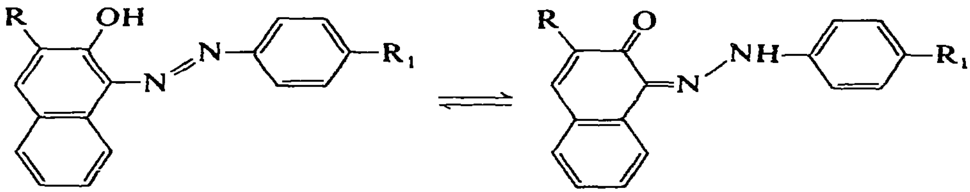
XXXIX Pigment Brown I

Monahan and Flannery[78] have indicated that intermolecular H-bonds are present in crystalline hydroxyazo compounds such as **II**(R = H), with the molecular structure being predominantly hydrazone. Whitaker[79] later proposed that azo pigments derived from **II** have a crystal structure consisting of hydrazone tautomers stabilized by intramolecular H-bonds and intermolecular Van der Waals forces.

Infrared spectral data for *o,o'*-dihydroxyazobenzene (**XXXX**) have indicated that both tautomers are present in the solid state,[80] and a conformational analysis of **XXXX** has taken this into account.[81]

3.4. *Gas phase studies*

From the few studies of gas phase tautomerism that have appeared in the literature it would seem that the absence of intermolecular interactions generally favours the azo tautomer. Only the azo tautomer of compound **XXXIV** has been observed in the gas phase.[57] A similar result was found for a number of monosubstituted derivatives of **II**,[82] although these compounds show hydrazone functionality in solution and in the solid state.[61,83] However, a recent report on the mass spectra of a number of azo dyes of general structure **XXXXI** has claimed to have detected ions arising from both azo and hydrazone tautomers.[84]



XXXXI

4. THE EFFECT ON TAUTOMERISM ON CHEMICAL REACTIVITY

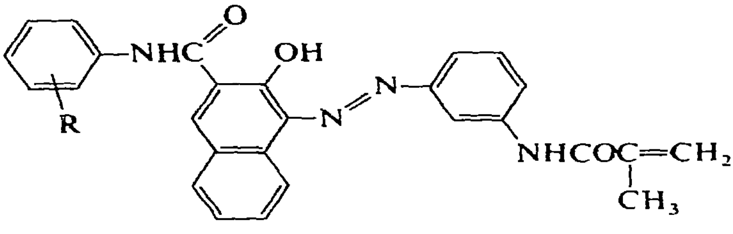
The fact that hydroxyarylazo compounds are capable of existing in either the azo or hydrazone form means that observed reactions will depend upon the tautomers present. A typical example is a report by Cardogan *et al.*,[85] who found that only the hydrazone tautomers of phenylazonaphthols were capable of nitrosation with *p*-chlorobenzoylnitrite. No reaction was observed for azobenzene of 4-phenylazo-1-methoxynaphthalene, which cannot exist as hydrazones.[85] Previously, Desai and Giles[86] had hypothesized that the initial step in the oxidation (by common oxidants) of azo dyes in aqueous media was one of hydrolytic attack on the C═N bond of the hydrazone tautomer of the dye. Other reports discuss such properties as charge transfer,[87] metal complexation[88,89] and chelation[90] with regard to azo–hydrazone tautomerism.

4.1. *Photochemistry*

Because of the widespread application of the hydroxyarylazo compounds as dyes and colourants, many studies of the chemical reactivity of the tautomeric systems have been concerned with their photofading. Griffiths and Hawkins have suggested that a reaction between singlet excited oxygen and the hydrazone tautomers of dyes of the general structure of **I** and **II** is responsible for their photodegradation.[91–93] Kuramoto and Kitao[94] reached the same conclusion after studying the photofading of a number of substituted azo dyes (**II**) in methanolic solution, although they later reported that compounds **II**, R = *o*- or *p*-NO_2, may fade reductively.[95] Mallet and Newbold[96] have maintained that reduction of the hydrazone form is the most important mechanism leading to the photodegradation of phenylazo-*β*-naphthol dyes (**II**) on polypropylene. In spite of this, these workers did note that oxidation was possible, especially when oxygen was available.[96] Previously, van Beek *et al.*[97] had suggested the possibility of photoreduction of both tautomers of hydroxyarylazo dyes in aqueous and ethanolic solutions by H-abstraction from a suitable donor (e.g. D,L-mandelic acid). However, Kitao *et al.*[98] surmised that the hydrazone tautomer was more susceptible to photodegradation because the photofading resistance of *o*-hydroxyazobenzene (**X**) decreased upon annellation of the phenol portion of the molecule (i.e. increase in proportion of hydrazone tautomer present).

Hempel *et al.* examined the fading of dyes of general structure **I**, **II** and **III** (R = *p*-substituent) in polyamide films and fibres[20,74] and reported that the substituents, R, influenced the rate of fading of the tautomers. The fading rate of the azo form of **I** (R = *p*-substituent) was increased by electron donating substituents (R), while that of the hydrazone tautomer was increased by electron acceptors.[20]

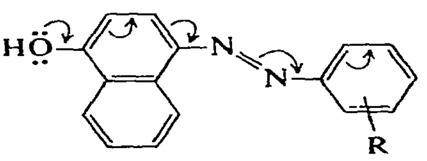
Although a chemical reaction might be specific to a particular tautomer, it would proceed to completion if carried out in solution due to the ability of the equilibrium to adjust as one tautomer is consumed. However, in substrates where the tautomeric forms are separate and immobile, and therefore incapable of interaction, one should observe a change in the state of the equilibrium as a tautomer-specific reaction proceeds. Such a situation was reported by Inukai,[99] who studied the fading of dyes **XXXXII** and their oligomers (d.p. = 2–10) in poly(methyl methacrylate) film.



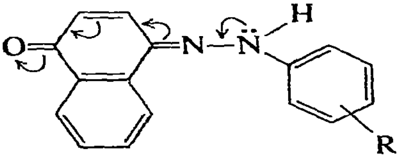
XXXXII R = H, *m*-NO_2, *o*-CH_3, *o*-OCH_3, *p*-Cl

For the oligomers (which faded more rapidly than the monomeric dyes), the proportion of hydrazone tautomer decreased markedly as fading progressed. However, the tautomeric equilibrium remained at a virtually constant level in the case of the monomeric dyes, in spite of their incorporation in the solid polymer substrate.

Another form of photochemical difference between the tautomers of phenylazonaphthols has been described by Griffiths.[100] He classified both tautomers of these compounds as 'donor–acceptor chromogens'. However, the direction of charge migration that accompanies electronic excitation to the first excited state is different for each tautomer. This is demonstrated in the diagrams below by the arrows which show the direction of charge migration for excitation to the first excited state.



I Azo tautomer



I Hydrazone tautomer

Griffiths has also shown that for a dye which can exist in two forms in equilibrium, the frequency difference between their visible absorption bands exhibits a linear relationship with Hammett σ substituent constants.[101] He demonstrated this dependence with the azo–hydrazone tautomeric forms of a number of substituted 4-phenylazo-1-naphthols (**I**).

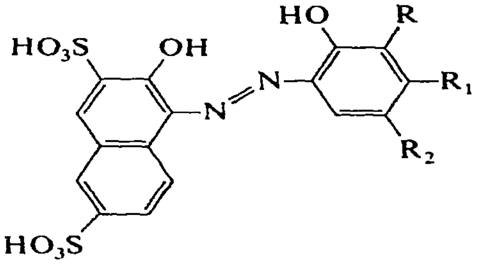
4.2. *Photochromism*

A well-known photochromic reaction of azo compounds is *trans*→*cis* isomerization.[1,102] For hydroxyazo compounds capable of azo–hydrazone tautomerism, the photochromic *trans* → *cis* isomerization depends on the state of the tautomeric equilibrium. The nitro derivative **II** (R = *p*-NO_2) exists almost completely in the hydrazone form and thus shows no photochromic behaviour.[13]

Fischer and Frei[103] observed that the *trans* isomer of the azo tautomer of I(R = H) could be converted to the less stable *cis* form when its alcoholic solution was irradiated at −140 °C. Upon warming (−135 → −90 °C), the *cis* isomer thermally reverted to the *trans* form via the phenylhydrazone tautomer. The hydrazone form could not be implicated in any direct photoconversion.[103]

Trans → *cis* isomerization of the azo form of II(R = H) has been studied by a dual-beam picosecond absorption spectroscopic technique.[104] The time constant for the reaction was found to increase with increasing solution viscosity.

The photoinduced *trans* → *cis* isomerization of the dyes **XXXXIII** has been studied by Russian workers.[105,106] Activation energies at pH > 10 varied from 5·7 to 23·6 kcal/mol, but these values could not be correlated with the nature or position of the substituents.[106]

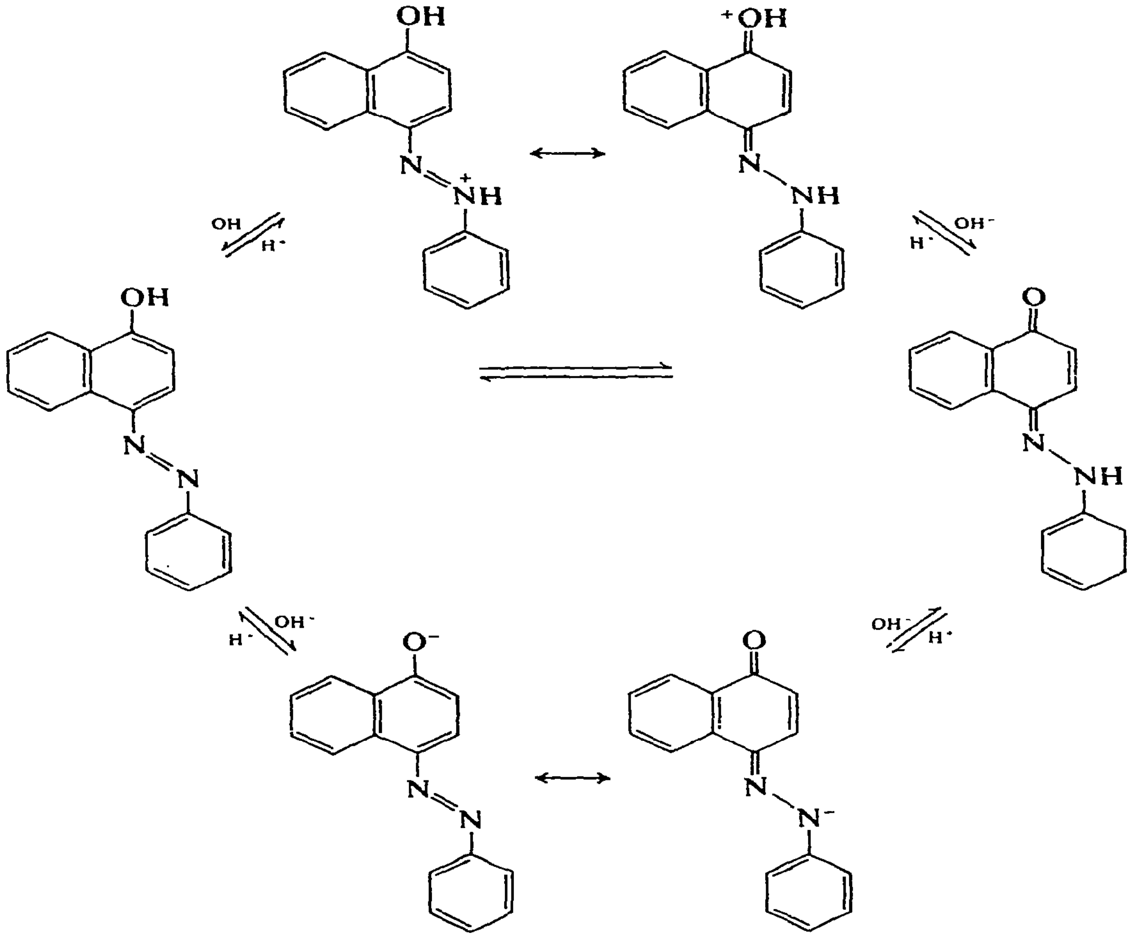


XXXXIII

4.3. *Acid–base behaviour*

The protonation equilibrium of a tautomeric compound is exemplified by I(R = H) in Scheme 4. In alkaline conditions, hydroxyarylazo compounds are capable of behaving as weak acids. The presence of a strong intramolecular H-bond in the case of the *ortho* derivatives (e.g. **II**) makes them much weaker acids than their *para* isomers (e.g. **I**). Griffiths[101] has suggested that at high pH each tautomer ionizes to a common anion as shown in Scheme 4. However, Trotter[107] used laser-Raman spectroscopy with supportive IR spectroscopy to examine a number of hydroxyazo compounds (including **I** and **II** (R = H)) in acidic and basic aqueous media and reported that at pH = 12 the ionized molecules had the form of the azo anion. Saito *et al.*[108] have claimed that in basic conditions, the anion of **I** and **II**(R = H) does exist as a resonance hybrid, but that the azo form of the anion is the more favoured canonical form.

Reeves[109] proposed that the protonated phenylazonaphthols exist as resonance stabilized azonium ions (see upper Scheme 4). However, a theoretical study by



I, R = H

Scheme 4

Bigelow[110] has shown that for 2-naphthol derivatives (**II**) the protonated hydrazone is the more likely form of the azonium ion.

Simov *et al.*[111] reported that spectrophotometric data and pK_a values of 16 *o,o'*-dihydroxyazo dyes indicated a tautomeric equilibrium for the dyes examined. Schreiber *et al.*[112] found a linear relationship between the pK_a of dyes of general structure **I** and the Hammett constant σ of the substituents R. Deviations from this relationship in the case of **I**(R = *p*-CN, *p*-CH_2CH_3, *p*-SO_2CH_3 and *p*-NO_2) were ascribed to a high concentration of hydrazone tautomer.[112] It has been shown that the azo form is more acidic than the corresponding hydrazone tautomer.[66,67]

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