

## Colour and Constitution Relationships in CI Acid Red 138 and its Homologues

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### ABSTRACT

*The potentially tautomeric acid azo dye CI Acid Red 138 and its homologues substituted by different alkyl groups were investigated by UV-Vis and PPP-MO techniques. The calculated  $\pi$ -electronic transition for the hydrazone form corresponds very closely to the experimental absorption spectrum. The observed negative solvatochromic effect is explained using the calculated dipole moments of the ground and first excited singlet states. The calculated transition moments are in opposite directions for both tautomeric structures, suggesting a specific substituent effect depending on which tautomeric form predominates. The observed low intensity fluorescence is assigned to the fluorescence ability of the hydrazone structure. The long wavelength band determining the colour is composed of discrete vibronic transitions, the relative intensities of which can change when particular chemical interactions between a dye molecule and its environment occur.*

### INTRODUCTION

The prediction of the light absorption properties of organic dyes is of theoretical and technological interest, and the PPP-MO method has proved to be a valuable tool for colour and constitution studies, and for the prediction and interpretation of the UV-Vis absorption spectra of organic molecules such as azo dyes.<sup>1-3</sup> In many cases the interaction of the dye with its environment, e.g. solvent,<sup>4,5</sup> dye,<sup>6,7</sup> surfactant,<sup>8</sup> macromolecule,<sup>9</sup> and other additives, e.g. cyclodextrins,<sup>10,11</sup> leads to a

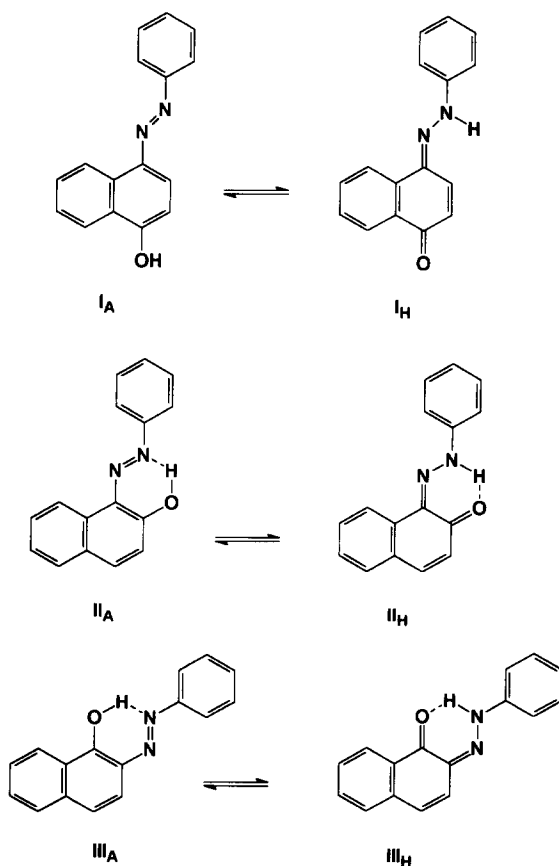
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change of the absorption spectra. Based on the spectral changes, the mechanism of the interactions has been discussed.<sup>12</sup>

The azo dyes are the most important class of commercial dyes and about 50% of commercially disclosed structures contain a naphthol ring.<sup>13</sup> In the case of phenylazonaphthol dyes (I–III) two tautomeric structures are possible, viz. azo (A) and hydrazone (H) (Scheme 1).

The shift of the  $A \rightleftharpoons H$  equilibrium in some tautomeric phenyl-azo-naphthol dyes, and a change of the equilibrium position with the environment, including the effect of solvent, are of great interest and have been investigated by spectral and quantum chemical techniques.<sup>3,13–19</sup> Which of the tautomeric structures is dominant under certain conditions is important for the colouristic and technological properties of these dyes.

To investigate further the  $A \rightleftharpoons H$  equilibrium of azo dyes, this report deals with some potentially tautomeric acid azo dyes, i.e. CI Acid Red 138 and its homologues containing different alkyl substituents.



Scheme 1

The use of the quantum chemical PPP-MO approach for the interpretation of the electronic transitions and  $\pi$ -electronic structure of azo and hydrazone tautomeric forms allows a prediction to be made of the spectroscopic differences between the two forms,<sup>14-16</sup> and conclusions to be reached regarding the important characteristics of the tautomeric structures which determine the colouristic properties.

## EXPERIMENTAL

### Materials

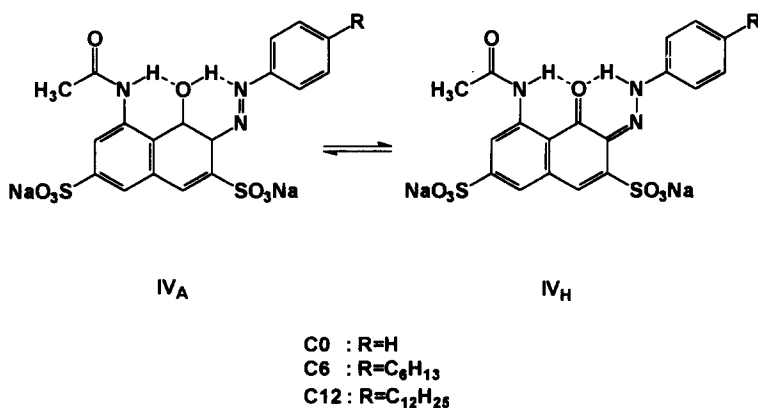
The dyes of structure **IV** were used. These dyes potentially exist in the tautomeric forms as shown in Scheme 2.

Dye **C12** (CI Acid Red 138) was obtained through purification of the commercially available dye by repeated salting-out with sodium acetate and extraction of sodium acetate with ethanol. Dyes **C6** and **C0** were synthesized from their respective intermediates and were purified by the same method.

The water used was purified by ion-exchange and distillation before use ( $<0.3 \mu\text{S cm}^{-2}$ ); ethanol, *n*-butanol and acetonitrile were of spectral grade (Merck or Fluka).

### Methods

The absorption spectra were obtained with a Lambda 17 UV/Vis Spectrophotometer (Perkin-Elmer) at constant temperature (20°C). Due to the low solubility of dyes **IV** in ethanol, *n*-butanol and acetonitrile the absorption spectra in these solvents were obtained at arbitrary concentrations (about  $5 \times 10^{-5} \text{ M}$ ).



Scheme 2

**TABLE 1**  
 PPP-MO Parameters Used for the Calculation of Absorption Spectra of Potentially  
 Tautomeric Azo Dyes

| <i>Bond X-Y</i> | $r_{X-Y} (\text{\AA})$ | $\beta_{X-Y} (eV)$ | $VSIP_Y (eV)$ | $\gamma_Y (eV)$ | $Z_Y$ |
|-----------------|------------------------|--------------------|---------------|-----------------|-------|
| C=C             | 1.40                   | -2.39              | 11.16         | 11.13           | 1     |
| (aromatic)      |                        |                    |               |                 |       |
| N=N             | 1.23                   | -2.90              | 14.70         | 12.40           | 1     |
| =N—C            | 1.38                   | -2.40              | 11.16         | 11.13           | 1     |
| C—OH (free)     | 1.36                   | -2.60              | 32.90         | 21.47           | 2     |
| C—OH            | 1.36                   | -2.60              | 28.60         | 18.30           | 2     |
| (H-bonded)      |                        |                    |               |                 |       |
| C=O (free)      | 1.22                   | -2.46              | 15.00         | 14.29           | 1     |
| C=O             | 1.22                   | -2.46              | 17.70         | 15.23           | 1     |
| (H-bonded)      |                        |                    |               |                 |       |
| C=N             | 1.33                   | -2.48              | 15.00         | 14.03           | 1     |
| (hydrazone)     |                        |                    |               |                 |       |
| =N—NH           | 1.35                   | -2.42              | 18.00         | 9.50            | 2     |
| (hydrazone)     |                        |                    |               |                 |       |
| NH—C            | 1.38                   | -2.65              | 11.16         | 11.13           | 1     |
| (hydrazone)     |                        |                    |               |                 |       |
| C—NH            | 1.38                   | -2.75              | 21.90         | 11.75           | 2     |
| (amide)         |                        |                    |               |                 |       |

The quantum chemical calculations were carried out using a conventional PPP SCF-CI program, suitable for use on a personal computer. The relevant parameters are those used by Griffiths *et al.*<sup>3,20,21</sup> Values most suitable for the systems **I–IV** are listed in Table 1.

## RESULTS AND DISCUSSION

The absorption spectra of **IV** (**C12**) in solvents of different polarity are shown in Fig. 1.

Most probably, the shape of the most intense long wavelength  $\pi$ – $\pi^*$  electronic transition around 500–520 nm is due to discrete vibronic transitions forming its complete band envelope. A small negative solvatochromic shift of the long wavelength band is also observed (Table 2).

The absorption spectrum of **IV** in ethanol, together with the calculated transition energies, proportional to the calculated  $f$  values for both tautomeric forms, are presented in Fig. 2.

It is important to note that in such comparisons, solvent effects must be minimized, and the absorption spectrum of the model compound should be measured in a solvent of as low a polarity as solubility permits.

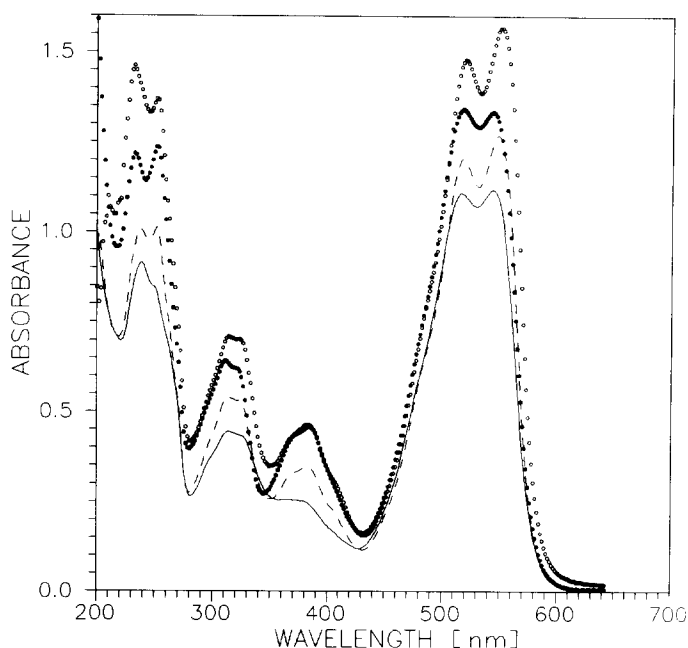


Fig. 1. Absorption spectra of IV (C12) in ethanol (---), water (—), *n*-butanol (oooo) and acetonitrile (●●●●).

The calculated electronic transitions for the **H**-form of IV correspond very closely to the experimental absorption spectrum and the calculated absorption maxima for the **A**- and **H**-forms of I–IV are at about 390–430 nm and 470–510 nm, respectively, in very good agreement with the corresponding experimental values and assignments.<sup>3,14,16,19,22</sup>

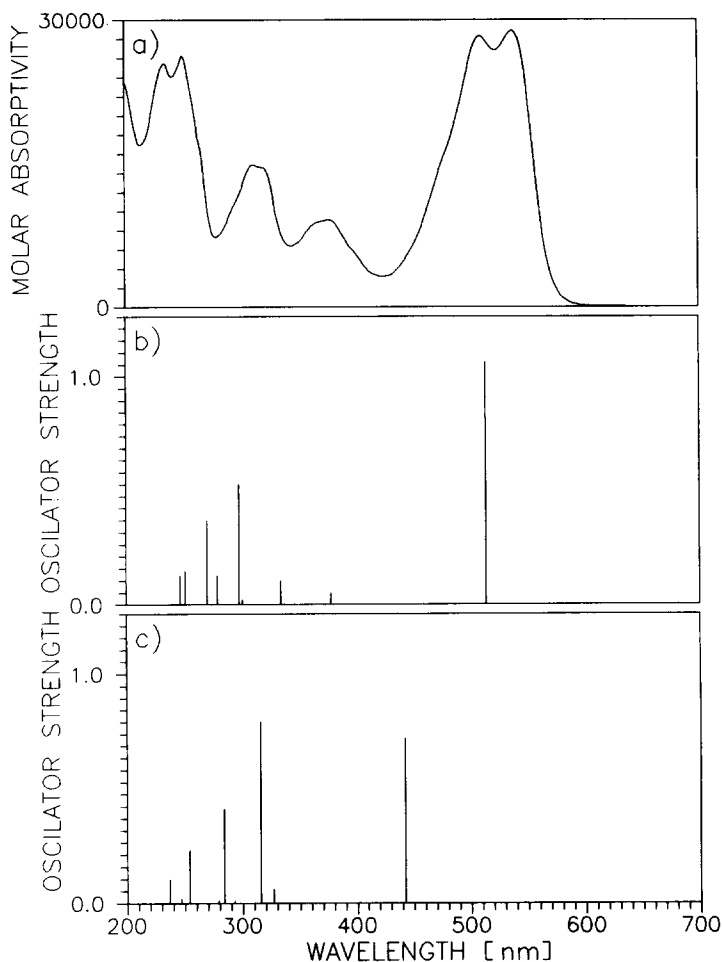
Further evidence that the **H**-form of IV is predominant comes from the calculated dipole moments ( $\mu^{\text{calc}}$ ) of the ground and first excited singlet

TABLE 2

Positions of the Two Main Vibronic Subbands in the Long Wavelength Band of Dyes C0, C6 and C12

| Solvent            | C0            |               | C6            |               | C12           |               |
|--------------------|---------------|---------------|---------------|---------------|---------------|---------------|
|                    | $\lambda_1^a$ | $\lambda_2^a$ | $\lambda_1^a$ | $\lambda_2^a$ | $\lambda_1^a$ | $\lambda_2^a$ |
| <i>n</i> -Butanol  | 548.0         | 509.6         | 557.6         | 516.0         | 557.6         | 516.8         |
| Ethanol            | 545.6         | 507.2         | 554.4         | 514.4         | 555.2         | 515.2         |
| CH <sub>3</sub> CN | 544.8         | 507.2         | 552.8         | 513.6         | 552.0         | 512.8         |
| H <sub>2</sub> O   | 539.2         | 501.6         | 551.2         | 511.2         | 552.0         | 512.0         |

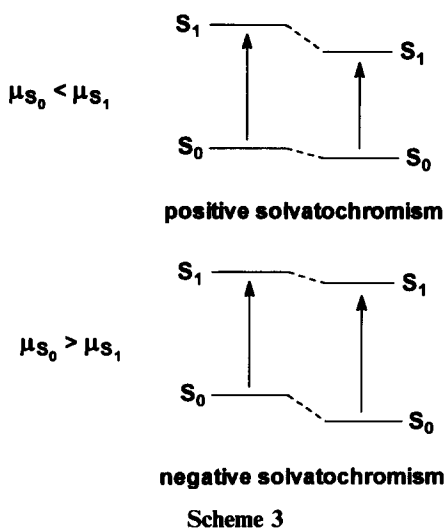
<sup>a</sup> Estimated from the second derivative spectra in the solvents used.



**Fig. 2.** (a) Absorption spectrum of IV (C0) in ethanol; (c), (b) calculated transition energies and oscillator strengths for both A- and H-tautomeric forms, respectively.

states. It was noted that a negative solvatochromic effect is observed (Fig. 1), i.e. increase in solvent polarity leads to a hypsochromic effect on the long wavelength maximum determining the colour of IV. This will be possible if  $\mu_{S_0} > \mu_{S_1}$ , leading to a greater stabilization of the ground state with increase of the polar environment of the molecule. The calculated values of  $\mu$  (Debye) are presented in Table 3, and only those for the H-form are in accordance with the above requirements. This effect is illustrated in Scheme 3.

In order to investigate the colour and constitution relationships of azo dyes, account must be taken of both states determining their colour, i.e. the ground state ( $S_0$ ) and the first excited singlet state ( $S_1$ ). The redistribution of the  $\pi$ -electron density during the  $S_0 \rightarrow S_1$  electronic transition



determines the influence on the colour properties of azo dyes of factors such as the effect of substituents, interaction of a dye molecule with its environment (solvent, polymer substrate, etc.) and the colour strength.

The change of the  $\pi$ -electronic density during the  $S_0 \rightarrow S_1$  transition can be illustrated schematically, showing the contribution of each atom in the charge transfer proceeding in both tautomeric structures **A** and **H**.

The differences between the calculated  $\pi$ -electron density  $\Delta Q_i = Q_i^{S_1} - Q_i^{S_0}$  for each atom  $i$  of both tautomeric structures are shown in Fig. 3, where the overall area of circles is proportional to  $\Delta Q_i$ . The solid circles correspond to an increase, and open ones to a decrease, of  $\pi$ -electron density upon the excitation of the molecule. The transition moment directions of the first electronic transition for both tautomeric structures are also given in Fig. 3.

In the case of the azo structure, the charge transfer during the  $S_0 \rightarrow S_1$  electronic transition proceeds mainly from specific sites in the naphthol ring towards the azo group, and in a smaller extent to the phenyl ring.

**TABLE 3**  
Calculated Dipole Moments ( $\mu$ , Debye) for Both  
Tautomeric Forms of **IV** in the Ground and First  
Excited Singlet States

| Structure | $\mu_{S_0}$ | $\mu_{S_1}$ |
|-----------|-------------|-------------|
| <b>A</b>  | 0.51        | 8.33        |
| <b>H</b>  | 3.14        | 3.05        |

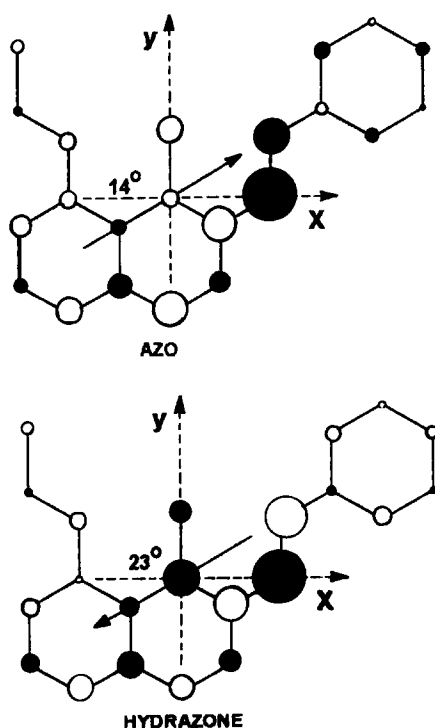


Fig. 3. Schematic presentation of  $\Delta Q_i$  for the two tautomeric A- and H-forms.

The opposite is true for the hydrazone structure, i.e. 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. For example, the introduction of electron donor or electron acceptor substituents into the phenyl ring (denoted by solid arrows in Fig. 3) will lead to a different effect depending on the position of the tautomeric equilibrium or which tautomeric form predominates. The same is true for substituents in the naphthalene ring. The effects of the substituents in I–IV can thus be explained and colour properties such as the hue of a dye with specific tautomeric structure can be projected.<sup>17,18</sup> In the case of IV, the introduction of an alkyl substituent into the *para*-position of the phenyl ring leads to a slight bathochromic effect of about 10 nm (Fig. 4).

It is interesting to note that the long wavelength absorption maxima of this series of dyes in aqueous solution shift to longer wavelength depending on the length of the alkyl chain. Values of 531, 540, 542, 543, 542, 543 and 543 nm for C0, C1, C4n, C4s, C6, C8 and C12, respectively, are observed,



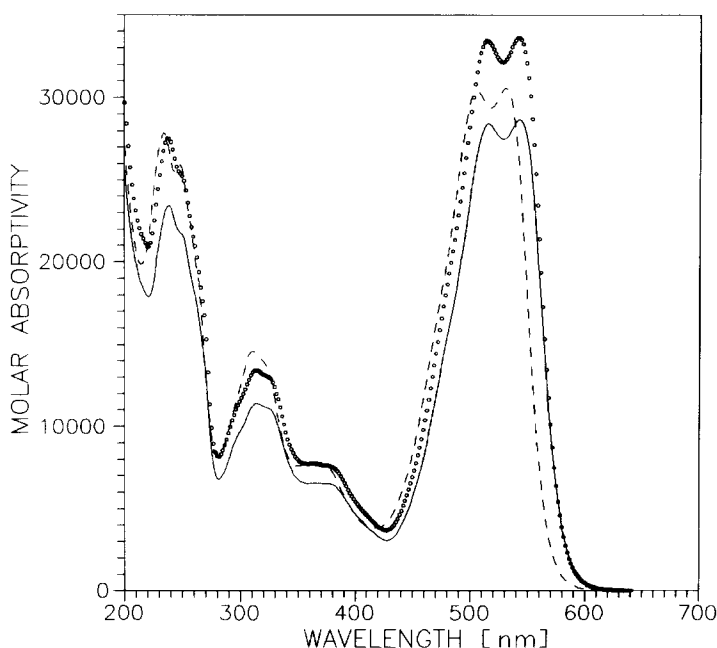


Fig. 4. Absorption spectra of **IV** in water: **C0** (---), **C6** (oooo) and **C12** (—).

where **C1**, **C4n**, **C4s** and **C8** denote the dyes with methyl, *n*-butyl, *s*-butyl and octyl groups, respectively.<sup>6</sup> The bathochromic shift could be explained only if the azo dyes **IV** exist predominantly in the **H**-form, since in this case, the alkyl substituent will enhance the polarization of the molecule (Fig. 3).

Evaluation of the influence of the alkyl group on the position of the long wavelength absorption band in the case of compounds **C0–C12** using the PPP-MO method is difficult, since the substituent is not directly involved in the  $\pi$ -electronic conjugation, and only the positive inductive effect should be taken into account. At this present stage, the concept of the hyperconjugation of the alkyl groups<sup>23</sup> is not involved in the calculations. Model treatment of this influence, changing the valence state ionisation potential (VSIP) value of the C atom directly connected with the alkyl group, revealed a very small bathochromic shift of about 2–3 nm in the calculated electronic transition, and almost the same value for the oscillator strength *f*.

Further support that the azo dyes **IV** exist in the **H**-form comes from the experimentally observed low intensity fluorescence of dyes **C0**, **C6** and **C12** in ethanol at about 590–600 nm, which could be assigned to the fluorescence ability of the hydrazone structure.<sup>19,24</sup>

With respect to the observed shape of the long wavelength absorption

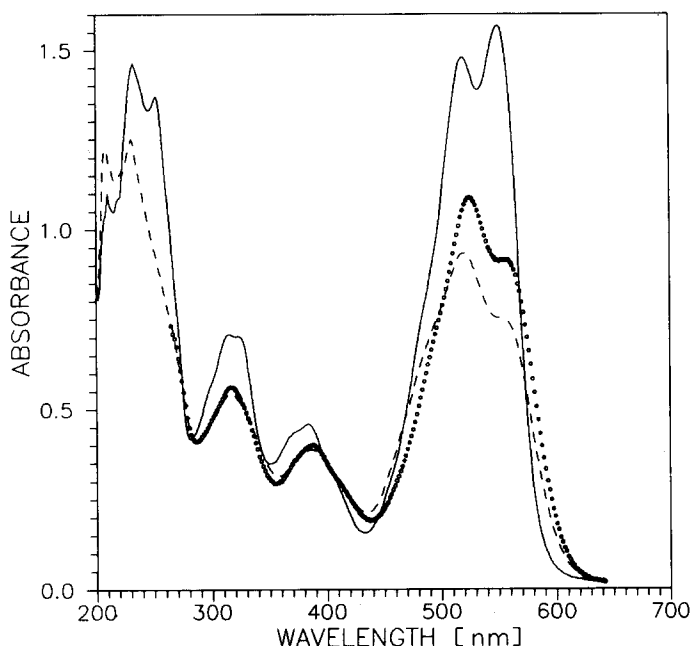


Fig. 5. Absorption spectra of IV (C12) in *n*-butanol (—); 50% *n*-butanol/ $\text{CCl}_4$  (oooo) and 50% *n*-butanol/*i*-octane (---), keeping the total dye concentration constant.

band (Fig. 1), it should be noted that the intensities of the discrete vibronic transitions depend on the overall equilibrium geometry difference between the ground state and the first excited singlet state of IV and its derivatives. When particular chemical interactions between a dye molecule and its environment occur, e.g. specific solvation or aggregation effects, they could change the equilibrium geometry of the  $S_0$  and  $S_1$  states, and hence a change in the relative intensities of the discrete vibronic bands within the long wavelength absorption band may occur (Fig. 5).

Such changes cannot be evaluated by the PPP-MO method, but some other experimental and computational approaches<sup>25,26</sup> can be used for such an evaluation.

## CONCLUSION

Application of the PPP-MO method to the investigation of colour and constitution relationships in potentially tautomeric azo dyes is a valuable tool for the interpretation of their absorption spectra and an evaluation of substituent effects, etc. The practically important acid azo dyes IV exist predominantly in the hydrazone form  $\text{IV}_H$  according to experimental

evidence and theoretical analysis. The higher value of the oscillator strength  $f$  for the H-form is in accordance with the effectiveness of these dyes as colouring agents. The chemical interactions between the dye molecule and its environment could change significantly the light absorption properties, e.g. shape and relative intensity of the discrete vibronic transitions within the long wavelength band, which determines the colour of these dyes.

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