

# Photophysics and Photochemistry of Azomethine Dyes

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## Abstract

In general the photochemistry and photophysics of azomethine dyes are characterised by: very broad and intense absorption bands, (band width  $\approx 100\text{nm}$  and  $\epsilon \approx 2\text{-}5 \times 10^4 \text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ ); high photostabilities, ( $\phi \approx 10^{-6}$  to  $10^{-7}$ ); very low room temperature fluorescence quantum yields, ( $\phi_f \approx 10^{-4}$  to  $10^{-5}$ ) which are enhanced at 77k to  $\phi_f \approx 0.001\text{-}1.0$  depending upon the dye type; low energy triplet states, ( $E_T \approx 94 \text{kJmol}^{-1}$  (cyan dyes) to  $200 \text{kJmol}^{-1}$  (yellow dyes)); short triplet lifetimes;  $\tau_T \leq 10 \text{ns}$ ; syn-anti isomerisation about the azomethine bond; and high rate constants for physical quenching of singlet oxygen, ( $k_q \approx 10^6\text{-}10^9 \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ ). Results from studies of two ballasted indoaniline cyan dyes confirm this general behaviour. For these cyan dyes  $\phi_n \leq 5 \times 10^{-5}$  in room temperature dibutylphthalate, triplet energies are  $87 \pm 4$  and  $94 \pm 4 \text{kJmol}^{-1}$ , and singlet oxygen quenching rate constants are  $6.6 (\pm 0.1) \times 10^9 \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ .

## Introduction

Azomethine dyes were first described by Seymour in 1934,<sup>1</sup> and they are commonly used in photographic products where they form the yellow, magenta and cyan images.<sup>2</sup> Despite the good light stability of these dyes, ( $\phi_{\text{photodegradation}} \sim 10^{-6}\text{-}10^{-7}$ ),<sup>3</sup> colour loss can still be noticed after prolonged exposure to ambient lighting. There is, therefore, a great deal of interest within the photographic field in the photochemical and photophysical properties of these dyes.

They are formed during development by the oxidative coupling of a p-phenylene diamine and the appropriate coupler (fig.1). Typical couplers are acylacetanilides which give yellow dyes [1]; 1,3-substituted-5-pyrazolones [2], and pyrazolo-triazoles [3] which give magenta dyes, and indols [4] which give cyan dyes. In this paper we will provide an overview of the photophysical and photochemical properties of these compounds along with results from our most recent studies on indoaniline cyan dyes.

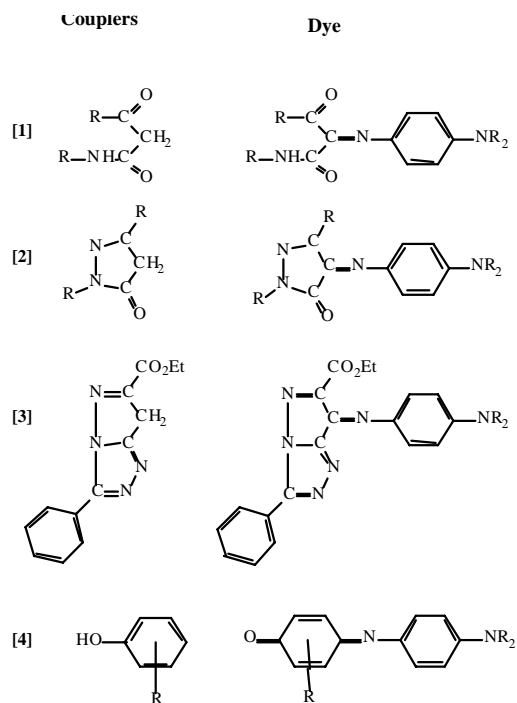


Figure 1. Couplers and dyes.

## Overview of the Photophysics and Photochemistry of Azomethine Dyes

### Singlet State Properties

**Absorption Characteristics.** In room temperature polar solvents the azomethine dyes have broad structureless, usually asymmetric, absorption bands in the visible spectral region with extinction coefficients in the region of  $2 - 5 \times 10^4 \text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ .

The pyrazolone azomethine dyes have two distinct bands,<sup>4</sup> an intense absorption in the green region (the x band) and a less intense band in the blue region (the y band), which is seen as a shoulder on the short wavelength

side of the x band. Smith<sup>4</sup> has shown that these arise from two different electronic transitions.

The pyrazolotriazole azomethine dyes have higher extinction coefficients, no secondary blue absorption and a sharper cut off on the long wavelength side.<sup>5</sup> The spectra of these pyrazolotriazole azomethine dyes show some structure in non polar solvents which has been shown to arise from a vibrational progression rather than additional electronic transitions; and thus these dyes show only one electronic transition in the visible spectral region.<sup>6</sup>

The effect of temperature on the absorption spectra of the pyrazolotriazole azomethine dyes has also been studied.<sup>7,8</sup> In a methanol-ethanol mixture decreasing the temperature gives a narrowing of the absorption band and a shift in  $\lambda_{\max}$  to longer wavelength. In methylcyclohexane with reducing temperature  $\lambda_{\max}$  is shifted to longer wavelength and a narrowing of the absorption band is seen, but at 213K a new absorption band is seen as a higher wavelength shoulder. As the temperature is reduced further this band increases in intensity at the expense of the lower wavelength band and shifts to longer wavelength. Low temperature spectra in poor solvents, such as methylcyclohexane, have proved difficult to understand perhaps because the behaviour arises from a combination of both solvent effects and aggregation.<sup>7</sup>

**Fluorescence Properties** Only a few papers on the excited singlet state properties of the azomethine dyes have been published,<sup>8,9,10</sup> and these focus on the pyrazolotriazole dyes. Douglas<sup>6</sup> showed that they have very low fluorescence quantum yields ( $\phi_f \sim 10^{-4}$ ) in room temperature solvents, results which would imply singlet state lifetimes of only a few picoseconds. Little change in the quantum yield of fluorescence is observed with either developer substitution or replacement of the methyl group at position 6 by hydrogen. However, emission yields from these dyes show a remarkable temperature/viscosity dependence and  $\phi_f$  increases to  $\sim 1$  in rigid organic glasses at 77K.<sup>8</sup> Room temperature picosecond absorption flash photolysis studies have identified a very short lived fluorescent state, along with a longer lived non fluorescent transient which is believed to be a twisted excited singlet state.<sup>8,9,10</sup>

**Triplet State Properties** Investigation of the triplet state of azomethine dyes has proven to be difficult. There have been no definitive reports of the direct observation of the triplet states of azomethine dyes. There are no reliable reports of phosphorescence or triplet state transient absorption from these dyes even though they have been studied by flash photolysis over timescales ranging from picoseconds to seconds.<sup>6-15</sup> A number of indirect methods have been used to determine triplet state properties.

Herkstroeter used an energy transfer method to investigate the triplet energies of a large number of yellow, magenta and cyan azomethine dyes. He obtained triplet energies of between 166 and 208 kJmol<sup>-1</sup> for the yellow dyes, but for cyan and magenta dyes he could only provide upper estimates of 87 and 96 kJmol<sup>-1</sup> respectively.<sup>13</sup> Later work on pyrazolotriazole azomethine dyes using the same method gave values of 100-120 kJmol<sup>-1</sup> for the triplet energies of these dyes.<sup>6,7,16</sup>

Again, using indirect methods, triplet lifetimes have been estimated to be less than 10 ns.<sup>6,16,17</sup>

It is interesting to note that azine dyes, (fig.2), for which flexibility around the azomethine bond is inhibited, show both low temperature phosphorescence and triplet-triplet absorption.<sup>13</sup>

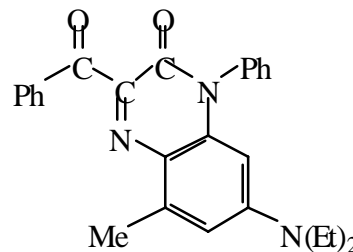


Figure 2. Azine dye.

It would appear from this that torsion about the C=N bond in the dye triplet manifold provides a pathway for rapid deactivation of the triplet state.<sup>13</sup>

### Isomerisation about the Carbon Nitrogen Double Bond

Compounds containing a carbon-nitrogen double can exist in either syn or anti configurations about the C=N bond (fig.3). Conclusive proof of isomerisation in azomethine dyes was provided by Herkstroeter.<sup>11</sup> Isomerisation can be brought about either by direct excitation of the dye or *via* triplet sensitisation. The room temperature lifetime of the unstable isomer depends upon dye structure and is generally of the order of a second or so for acylacetanilide dyes, and milliseconds to microseconds for pyrazolotriazole and pyrazolone dyes.<sup>6-15</sup>

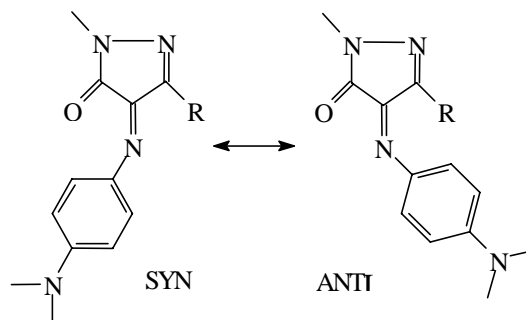


Figure 3. Syn and anti isomers of a pyrazolone azomethine dye.

There are three possible mechanisms for syn-anti isomerisation about the C=N double bond: (a) the torsion or twist mechanism (fig.4-[1]), (b) the linear inversion or lateral shift mechanism (fig.4-[2]), and (c) rotation about the C=N double bond.(fig.4-[3]). Which of these mechanisms is dominant for the azomethine dyes has been the subject of a number of studies of solvent, substituent, and pressure effects.<sup>10,12,14,15,18</sup> Taken as a whole these studies suggest that the isomerisation mechanism is dye dependent.

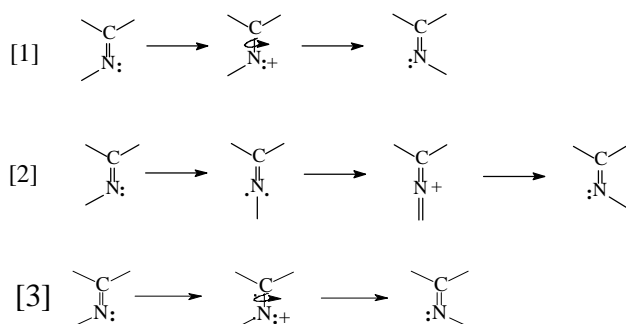


Figure 4. Mechanisms for rotation about the C=N double bond.

**Quenching of Singlet Oxygen** Azomethine dyes act as efficient physical quenchers of singlet oxygen.<sup>19</sup> Typically, magenta and cyan dyes quench singlet oxygen in low viscosity fluid solution with rate constants of  $\sim 10^7$  -  $10^9$  mol<sup>-1</sup>dm<sup>3</sup>s<sup>-1</sup>,<sup>16,19</sup> while rate constants for quenching by yellow dyes tend to be  $\sim 10^6$  -  $10^7$  mol<sup>-1</sup>dm<sup>3</sup>s<sup>-1</sup>. Smith *et al.* discussed the mechanism of this process and concluded that the variation in rate constants for the dyes studied could not be explained by a simple energy transfer step. They proposed a mechanism involving formation of an exciplex between the dye and singlet oxygen, in which either electron transfer or energy transfer causes stabilisation of the exciplex.<sup>19</sup>

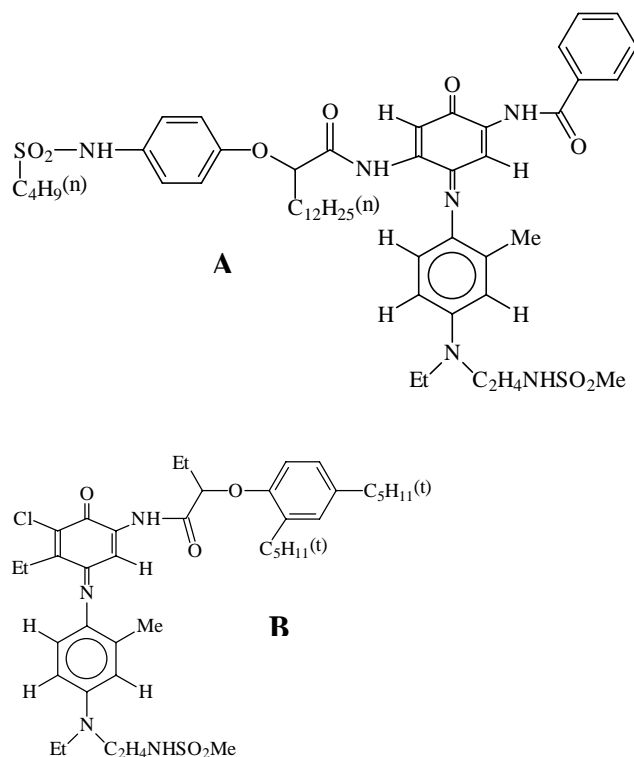


Figure 5. Cyan indoaniline dye structures.

## Results from Recent Work on Cyan Dyes

In our most recent work we have examined the photophysics and photochemistry of the two cyan dyes shown in fig 5.

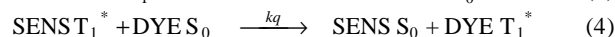
**Singlet State Properties** Table 1 gives two independently obtained sets of data giving; measured fluorescence quantum yields, radiative rate constants (calculated using the Strickler-Berg equation<sup>20</sup>) and estimated non-radiative rate constants and lifetimes for dyes A and B in dibutylphthalate.

Characteristic	Dye A		Dye B	
$k^{\text{rad}}/\text{s}^{-1}$	$1.0 \pm 0.02 \times 10^8$	$9.8 \pm 0.5 \times 10^7$	$8 \pm 0.9 \times 10^7$	$9.3 \pm 0.5 \times 10^7$
$k^{\text{n}}/\text{s}^{-1}$	$2.0 \pm 0.2 \times 10^{12}$	$1.7 \pm 0.3 \times 10^{12}$	$>8 \times 10^{12}$	$5.0 \pm 2.0 \times 10^{12}$
$\phi_{\text{fl}}$	$5.0 \pm 0.5 \times 10^{-5}$	$5.7 \pm 0.5 \times 10^{-5}$	$<1.0 \times 10^{-5}$	$1.8 \pm 0.5 \times 10^{-5}$
$\tau_s$	500fs	600fs	$<125$ fs	200fs

Table 1. Values for  $k^{\text{rad}}$  (radiative rate constant),  $k^{\text{n}}$  (non-radiative rate constant),  $\phi_{\text{fl}}$  and  $\tau_s$  (lifetime of the first excited singlet state). First column obtained by workers in Swansea, second by workers in Harrow.

## Triplet-Triplet Energy Transfer Measurements

Flash photolysis of these dyes in the absence of sensitiser produced no transient species on a microsecond or nanosecond time scale. In the absence of dye, flash photolysis of the sensitiser generates the sensitiser triplet state (SENS  $T_1^*$ ). Addition of dye leads to an increase in the rate of SENS  $T_1^*$  decay. In all studies with dye A and B no transients other than SENS  $T_1^*$  were observed, suggesting that electron transfer is unimportant and that the increase in decay of SENS  $T_1^*$  is caused by triplet-triplet energy transfer to the dye.



where ISC=Inter System Crossing; kr=rate constant for radiative decay; kq=rate constant for quenching; \*=excited state.

$$d[\text{SENS}]/dt = k_r[\text{SENS } T_1^*] + k_q[\text{DYE}][\text{SENS } T_1^*] \quad (5)$$

and

$$k_{\text{obs}} = k_r + k_q[\text{DYE}] \quad (6)$$

where  $k_{\text{obs}}$  = observed rate of decay of sensitiser triplet state.

From equation 6 it can be seen that the quenching rate constant can be found by plotting  $k_{\text{obs}}$  against the concentration of dye present. This gives a straight line with gradient  $k_q$ . As discussed by Herkstroeter<sup>15</sup> and Balzani<sup>21</sup>, a study of the variation in  $k_q$  with sensitiser triplet energy can

be used to measure the dye triplet energy. In essence energy transfer will occur with the same rate constant, (usually the diffusion controlled rate constant) for all triplet sensitiser with a triplet energy significantly higher than that of the dye, but once the sensitiser triplet energy approaches, or drops lower, than that of the dye the quenching rate constant is reduced. The triplet energies of all the sensitiser used are shown below in table 2.

Sensitiser	Triplet energy/ kJmol <sup>-1</sup>	Reference
<b>Pd TPP</b>	174	24
<b>Zn TPP</b>	153	25
<b>TPP</b>	139	24
<b>Zn P</b>	109	26
<b>CAP</b>	105	16
<b>N</b>	89.5	Calculated <sup>#</sup>
<b>GaN</b>	85.5	Calculated <sup>#</sup>
<b>SnN</b>	84.3	Calculated <sup>#</sup>

Table 2. Triplet energies of the sensitiser used. TPP = tetraphenylporphine, P=phthalocyanine, CAP=chloroaluminum phthalocyanine and N=Naphthalocyanine. (<sup>#</sup>Calculated assuming a constant singlet-triplet energy ratio)<sup>22</sup>

Figure 6 shows the results for dye A in chloronaphthalene. The analysis indicates a triplet energy of 94±4 kJmol<sup>-1</sup> for dye A. Similar studies with dye B give a triplet energy of 87±4kJmol<sup>-1</sup>.

**Syn-Anti Isomerisation** We have been unable to detect any transients due to syn-anti isomerisation for either dye A or dye B when using either direct or triplet sensitised excitation in flash photolysis studies over the nanoseconds to seconds timescale.

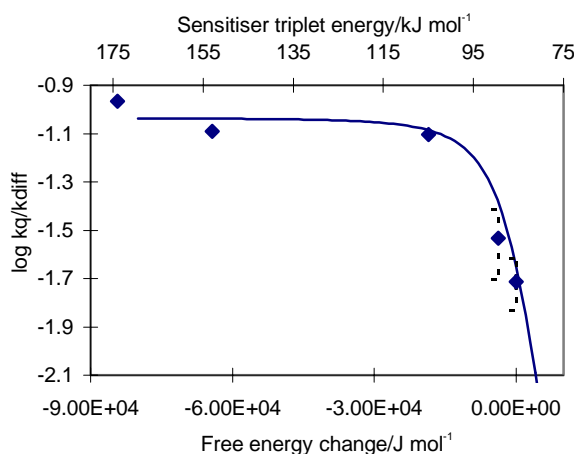
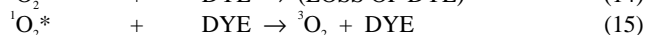
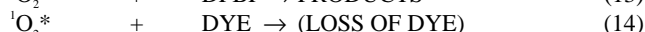
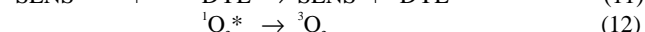
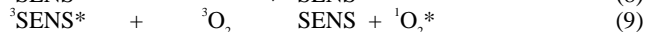


Figure 6. Analysis of triplet quenching data using the Balzani equation.<sup>21</sup>

**Singlet Oxygen Quenching Rate Constants** The rate of reaction of the dyes with singlet oxygen has been measured using a flash photolysis technique. The method relies on generating <sup>1</sup>O<sub>2</sub> using a sensitiser and then determining the rate of loss of a <sup>1</sup>O<sub>2</sub> acceptor in the

presence and absence of the dye. The laser pulse is used to generate a small concentration of <sup>1</sup>O<sub>2</sub> rapidly; subsequent reaction of which causes loss of the <sup>1</sup>O<sub>2</sub> acceptor, a process which can be studied directly over a period of a few microseconds. The reaction scheme and analysis are as follows<sup>(23)</sup>



Provided the concentration of DPBF stays effectively constant throughout any one kinetic run, after the decay of the sensitiser triplet (complete within 2μs or so), the observed first-order rate constant for the decay of [DPBF],  $k_{\text{obs}}$ , is given by:

$$k_{\text{obs}} = (k_{14} + k_{15})[\text{DYE}] + k_{13}[\text{DPBF}] + k_{12} \quad (16)$$

so that a plot of  $k_{\text{obs}}$  against [DYE] has a slope =  $k_{14} + k_{15}$ .

Anthracene was used as sensitiser and DPBF as <sup>1</sup>O<sub>2</sub>\* acceptor. The DPBF concentration was kept low to maximise the lifetime of <sup>1</sup>O<sub>2</sub>\* and only a small fraction of the DPBF present was consumed in the reaction to maintain simple kinetics.

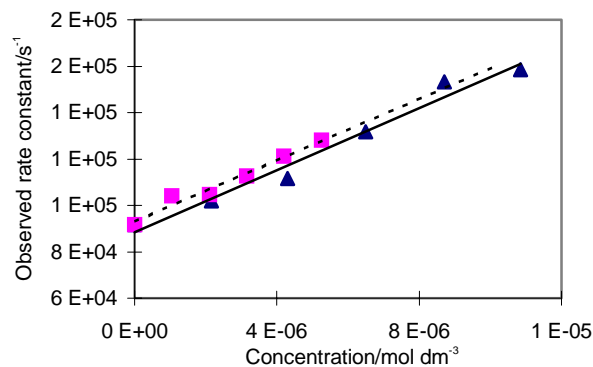


Figure 7. Determination of singlet oxygen reaction rates for dye A (squares), and dye B (triangles).

The data obtained for dyes A and B shown in figure 7 give reaction rate constants of  $6.7(\pm 0.5) \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  and  $6.5(\pm 0.5) \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  respectively. No loss of dye was detected in these experiments and thus  $k_{15} \gg k_{14}$ . We can therefore equate the experimental quenching rate constant with physical quenching by the dye, i.e.  $k_{15} = 6.6 (\pm 0.1) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

## Conclusion

The photophysical and photochemical behaviour of the cyan dyes A and B is generally in accord with what has been found previously for azomethine dyes. The combination of weak fluorescence and high absorption extinction coefficients for these dyes leads to calculated singlet lifetimes of at most a few hundred femtoseconds: 560 fs for dye A, and 200 fs for dye B. Triplet energies of the two cyan dyes are  $94 \pm 4$  kJmol<sup>-1</sup> and  $87 \pm 4$  kJmol<sup>-1</sup> for dye A and B respectively. The triplet energy of dye A is very close to that of singlet oxygen while the triplet state of dye B is somewhat lower than that of singlet oxygen. As expected for dyes with triplet energies in this range the rate constants for quenching of singlet oxygen by the dyes ( $6.6 (\pm 0.5) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>) are close to those calculated for diffusion controlled reactions. The failure to detect any evidence of photoinduced syn-anti isomerisation for these indoaniline cyan dyes is interesting. There are three possible explanations for this lack of detectable isomerisation: (1)-the quantum yield of isomerisation is very low for both direct and triplet sensitised isomerisation; (2)-the isomer lifetime is less than a few tens of nanoseconds; (3)-the syn and anti isomers have experimentally identical absorption spectra. At present we do not know which of these, or combination of these, is responsible for the lack of detectable isomerisation.

## Acknowledgements

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