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A study on the behaviour of photochromic acid and disperse dyes on dyed textile and leather substrates using colour measurement techniques and a semi-empirical approach to explain the observed phenomena

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ABSTRACT

Spirooxazine-based photochromic acid and disperse dyes have been synthesized and applied for the dyeing of textile (such as, nylon) and leather substrates. The dyed substrates show photochromic colour build up (from a colourless state to a coloured state) when exposed to UV light or sunlight. In this paper, the nature of two selected spirooxazine based photochromic dyes (one is a disperse dye type and the other one is an acid dye type of structure) in terms of photochromic colour build up on dyed textile and leather substrates are evaluated using specifically developed colour measurement techniques. A variation was observed on the photochromic colour build up (after exposure to UV light) with a change in the nature of the substrate and thedye type used. As a result a semi-empirical approach (such as, AM1, AM1 in water, PM5, PM5 in water, ZINDO) was used to analyse some of these observed behaviours based on the calculated electronic properties of these two dyes at a molecular level.

Keywords: *Spirooxazine, photochromic textile and leather, colour measurement, semi-empirical approach.*

1. INTRODUCTION

Photochromic dyes are used for various purposes, such as – in non-linear optics, security printing and optical data storage. These functional dyes can be used for the coloration of different textile and leather substrates in order to use them for a number of potential applications including – (a) authentication, (b) applications as sensors, (c) camouflage, (d) UV warning systems, (e) brand protection, (f) applications in fashion and novelty products [1-15]. In general terms, photochromic dyes show reversible transformation from a colourless to a coloured state under UV irradiation. They are of two types – (a) organic (such as spirooxazines, spiropyrans, chromenes, diarylethenes) and (b) inorganic (such as metal dithizonate, titanium dioxide, silver halide). Spirooxazines show high fatigue resistance which attract current active research interest for various potential applications [1-10]. A spirooxazine contains a spiro carbon atom which is sp^3 hybridized and serves to separate the molecule into two halves; each half is comprised of benzenoid heterocyclics whose π-systems are orthogonal and thus are not conjugated across the spiro-carbon atom. As spiro-carbon atom separates the localized π-systems, all absorptions occur in the ultra-violet rather than the visible region of the spectrum. Thus, the spirooxazine is colourless in its unactivated form. The oxazine bridge between the oxygen and the spiro-carbon atom of the spirooxazine is ruptured upon exposure to UV radiation [1-10]. The molecule undergoes a geometric rearrangement and form an open merocyanine form where the π-systems is conjugated along the entire molecule that is virtually planar. This conversion lowers the energy of the transition, and thus, the molecule absorbs at longer wavelengths, i.e., in the visible region of the spectrum. Upon exposure to a UV source, compound **1** in solution or in a suitable solid matrix produces a blue color [1-10]. Again, when the UV source is removed the molecule relaxes from its excited state and reverts to its original geometric conformation, i.e. the closed form in which the oxazine bridge is re-established. Figure 1 illustrates the ring opening reaction of a spirooxazine **1** (which has a disperse dye type structure).

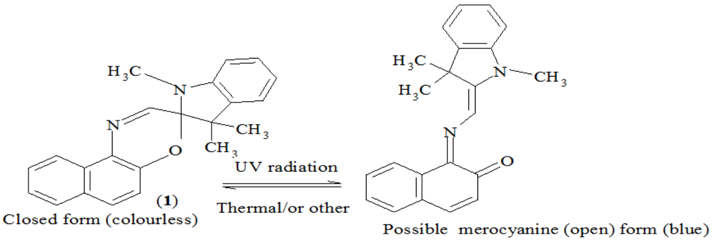


Figure 1. The photochromic conversion of a spirooxazine from its colourless closed form to its one of the possible coloured photomerocyanine form (which produces blue colour under UV light) when exposed to UV light or sunlight. It also represents the nature of the ring opening reaction of spirooxazine **1**.

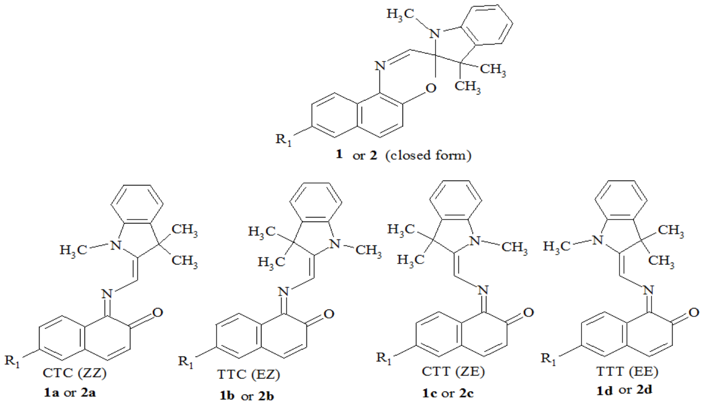
So far one of the most prominent applications of photochromic dyes are in the field of ophthalmic lenses, security printing and optical data storage. Very little attention have been paid to designing the dyes for direct application to textiles and leather, for functions such as authentication, sensors, and camouflage as well as for fashion and novelty. A series of spirooxazine-based photochromic acid dyes have been synthesized in our laboratories, selected based on molecular design using a range of molecular modeling methods for the prediction of photochromic behaviour and selectively a number of them have been used to the coloration of textiles and leather. Nylon, a polyamide based textile substrate provides the opportunity to dye it with both photochromic acid dye (**2**) and photochromic disperse dye (**1**). Both of these dyes **1** and **2** were used to dye the nylon substrate. A comparative study revealed that the nylon sample dyed with photochromic acid dye **2** (N2) showed marginally higher photochromic colour build up under UV irradiation then the nylon sample dyed with photochromic disperse dye **1** (N1). In addition, a leather substrate (full chrome white crust leather from goat skin origin) was dyed with dye **2** which showed relatively less photochromic colour build up on dyed leather substrate under UV irradiation compared to the photochromic colour build up on nylon dyed with dye **2** at a similar application condition. Semi-empirical molecular machanics (such as MM2) and quantum mechanical (AM1, AM1 in water, PM5 and PM5 in water) minimisation techniques were used to investigate this phenomena at a molecular level. This paper discusses the colour measurement results and also provides an analysis of these results with the help of calculated electronic properties (obtained from the use of semi-empirical studies) of these two dyes at molecular level.

2. EXPERIMENTAL SECTION

Spirooxazine dyes **1** and **2** were synthesized using methods described previously [1, 3]. Details of the dyeing methods [1, 4], colour measurement techniques and molecular modelling techniques used in this current study have been reported in previous communications [2-5].

3. RESULTS SECTION

Molecular modelling was used for the prediction of spectral properties and of photochromic behaviour on the basis of calculation of energies. A series of spirooxazine-based photochromic acid dyes were synthesized by incorporating water-solubilising functionality into the structure of the parent photochromic spirooxazine disperse dye **1,** based on the molecular modelling information. These new photochromic acid dyes were selectively used to dye suitable textile and leather substrates. This paper describes the behaviour of photochromic acid dye **2**, comparing its performance with photochromic disperse dye **1** when used for the dyeing of nylon and a comparative photochromic colour build up performance of the dye **2** in nylon and in leather substrates. The usefulness of the application of a range of molecular modelling methods available within the CAChe software package for the prediction of photochromic and spectral properties of spirooxazines have been published in the previous reports [2, 4].



1: $R_1 = H$; **2**: $R_1 = SO_3^-$

Figure 2. Four possible transoid open (photomerocyanine forms) of spirooxazine-based photochromic dyes **1** and **2**.

The final energies of the colourless closed forms **1** and **2** are lower than those of their respective four transoid photomerocyanine isomers and this is true also for heats of formation calculated using AM1 and PM5 [2, 4]. The results are consistent with observed behaviour on dyed nylon and leather substrates which show photochromic colour change from a colourless (or weakly coloured) state to blue coloured state when exposed to UV irradiation (Figure 3). Detail explanations of the relation between computation study and observed solid state photochromic colour build up phenomena have been provided in previous papers [2, 4].

Figure 2 demonstrates the four possible transoid open or photomerocyanine forms of spirooxazine based photochromic dyes **1** and **2**. When exposed to UV light or sunlight both of these two dyes may transform from their colourless (perpendicular geometric structures) state as in **1** and **2** to their possible transoid photomerocyanine forms (**1a** to **1d** and **2a** to **2d**). Detail of the conversion mechanisms have been reported elsewhere in previous papers [1-10].

Figure 3 illustrates the photochromic colour build up on nylon sample dyed with dye **2** (N2) is marginally higher than another nylon sample dyed with dye **1** (N1) which could be attributed to a number of factors including relatively higher uptake of dye **2** than dye **1** in the nylon fabric samples dyed with a similar equivalent concentration level using these two dyes. Another important factor is dye **1** was applied in dispersed form where the presence of the dispersant might have some impact on the nature of total dye uptake in the case of N1.

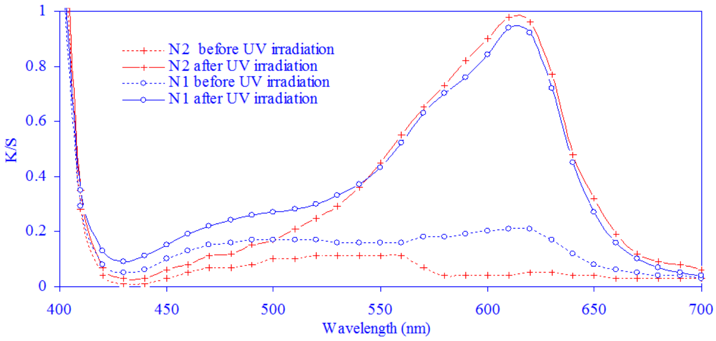


Figure 3. Photochromic colour build up on nylon sample dyed with dye **1** (N1) and another nylon sample dyed with dye **2** (N2).

Figure 4 demonstrates the nature of photochromic colour build up on the leather substrate dyed with dye **2** (SPO 2) after exposure to UV light. From the analysis of the colour build up on nylon in Figure 3 and the colour build up on leather in Figure 4, it is clear that there is relatively higher photochromic colour build up on nylon than on the leather substrate. This phenomenon can be ascribed to a number of factors including the matrix dependent photochromic colour build up of photochromic dyes [1-14].

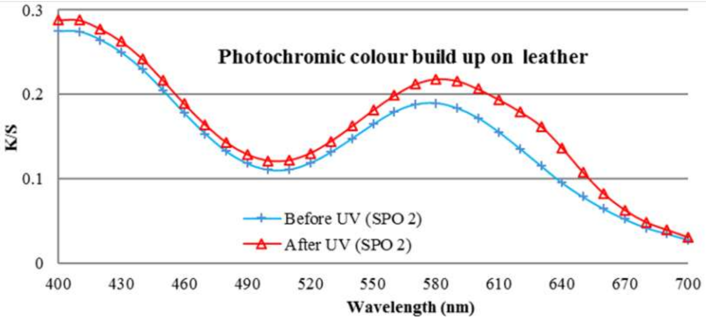


Figure 4. The nature of photochromic colour build up on leather dyed with dye **2** (also termed as SPO 2) after exposure to UV light.

In order to explain the feature of a relatively higher level of photochromic colour build up on nylon N2 dyed with dye **2** than the nylon sample N1 dyed with dye **1** the electronic properties of these two dyes have been rigorously studied which are presented in Tables 1 and 2 and Figures 5 and 6.

Dipole moments were simultaneously calculated during the calculation of final heat of formations using the semi-empirical minimisation techniques AM1 and PM5 (Table 1) [2, 5]. Calculated results show that the dipole moments for compound **2** are relatively higher than from compound **1** in the gaseous phase for both open and closed forms. These results confirm that due to higher polarity in dye **2** it may have a positive contribution to influence the chemical affinity of this dye for the polyamide (nylon) substrate and hence there is a variation with the results in photochromic colour build up in nylon samples N1 and N2 dyed with dyes **1** and **2** respectively.

Table 1. The dipole moments of dyes**1** and **2** in gaseous phase from AM1 and PM5 calculations.

Structure	Dipole moment (debye)	
	AM1	PM5
1 (closed form, ground state)	1.17	2.01
1b (one of the most stable photomerocyanine state)	1.81	2.55
2 (closed form, ground state)	27.65	28.92
2b(one of the most stable photomerocyanine state)	25.10	25.03

Additionally, when exposed to UV light spirooxazines become excited (from colourless ground states) and proceed through metastable transition states until they reach in relatively stable photomerocyanine states with possible lowest energy levels [2, 5-19]. In this case, as the spirooxazines (**1** and **2**) show dynamic colour change so the nature of change of dipole moment with the change in the electronic state due to π-electron conjugations in the two halves of the non-planner spirooxazine molecules **1** and **2** may provide some important information. It may be used to explain the relatively marginally higher colour build up on the nylon fabric dyed with **2** compared to the nylon fabric dyed with **1**. Figure 5 illustrates the transition energies and transition dipole moments for different transition electronic states of dyes **1** and **2** while Figure 6 exhibits the transition energies for different transition electronic states of dyes **1** and **2**.

The PM5 and PM5 in water calculations on dyes **1** and **2** also allow to calculate the transition dipole moments of several prominent electronic states. In this study, 64 most prominent transition states were calculated which are also termed as electronic states, and each states show a single transition dipole moment. The energies of different transition states are expressed with respect to the wave functions and energy units in cm^{-1}. In most of the cases the transition dipole moments for dye **2** is marginally higher than the transition dipole moments of dye**1** both in PM5 and PM5 in water calculations (with exception, electronic states 29-40, 57-64). Although, this transition dipoles results are unable to provide an conclusive evidence, but the usual dipole moments (static dipole moments) provide a more conclusive evidence that the dipole moments of closed and open photomerocyanine forms of dye **2** are always high compared to the similar dipole moments of the closed and open photomerocyanine forms of dye **1** (Table 1). This implies that due to the introduction of SO_3^- group into the structure of dye **1** to produce dye **2**, provides a significant structural change making dye **2** more prone to a strong dipolar interaction, in addition to the interaction due to van der Waals forces similar to dye **1** as both of the dyes **1** and **2** are structurally large molecules. Thus, the interaction between dye **2** and the dyed nylon fabric is relatively more intense than from the interaction between the dye **1** and the dyed nylon fabric. It is consistent with the previously reported results of the stronger technical performances of nylon fabric dye **2** from the nylon fabric dyed with **1**, when the nylon fabric dyed with these two dyes in similar strength [1, 7].

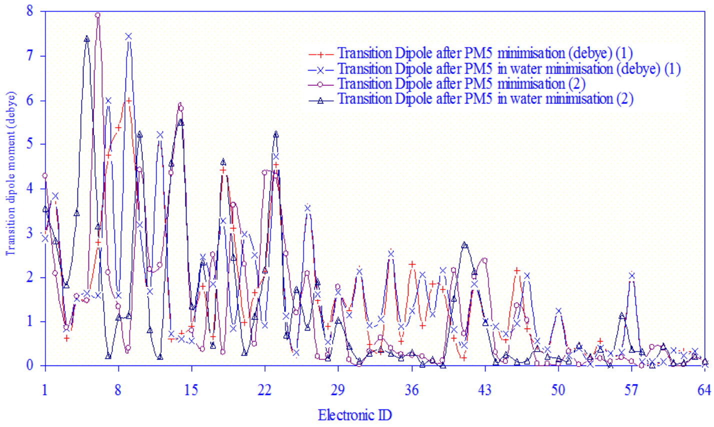


Figure 5. Transition energies and transition dipole moments for different transition electronic states of dyes **1** and **2**.

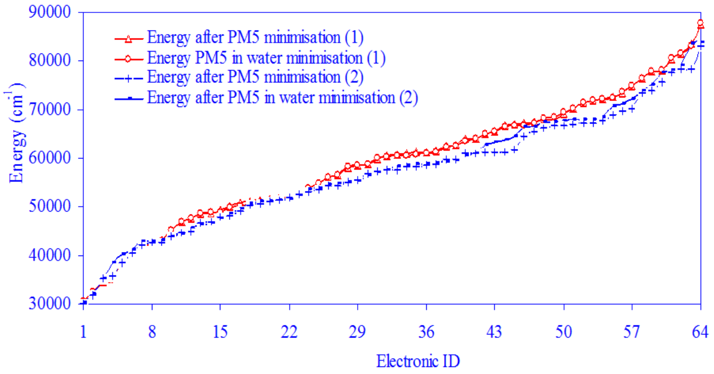


Figure 6. Transition energies for different transition electronic states of dyes **1** and **2**.

Thus, the different reasons of the marginal higher colour build up in nylon fabric dyed with **2** (N2) than from the nylon fabric dyed with **1** (N1) may include these two main reasons: (a) dye **2** is highly polar (Table 1) so there is a possibility that it has relatively very high dipole-dipole interaction, which may allow a further advantage to dye **2** for higher dye –fibre interaction and also a higher dye up take and hence marginal higher colour build up; (b) the hydrophobic interaction between dye **1** and dye nylon fabric (N1) is relatively less strong than a cumulative joint force (due to dipole-dipole interaction, hydrogen bond and van der Waals force) of interaction between dye **2** and the dyed nylon fabric (N2).

In addition, the electronic properties along with some other properties of spirooxazine dyes **1** and **2** are envisaged to provide some further information to explain the situation (Table 2) which shows a clear variations on different electronic properties of these two dyes that can have many impacts on their chemical affinities and other related properties. The results obtained from the calculation of the electronic charges or the electronic energies of compounds **1** and **2** at different molecular levels also confirm a strong possibility of more potential for interaction for dye **2** and then from dye **1** with dyed nylon fabrics, which might have assisted dye **2** to interact more rigorously with the dyed nylon with a higher dye uptake and hence there is a relative higher colour build up in N2. Although, the photochromic colour build up is matrix dependent but still the explanation of this observed fact of higher colour build up in N2 using the calculated molecular modeling results provide some insights on molecular level understanding on this phenomenon.

Besides this, photochromic colour build up is a function of a number of factors, including the dye structure, the matrix and the surrounding environment, where all of them play a very significant role [10-19].

Table 2. Different properties of dyes **1** and **2** obtained after AM1 minimisation followed by ZINDO calculations.

Calculated electronic properties	dye**1**	dye**2**
Total energy (ev)	-3823.85	-4972.36
Electronic energy (ev)	-30588.10	-38992.83
Core-core repulsion (ev)	26764.25	34025.03
Molecular weight	328.41	407.46

The nature of color build up on textile and leather substrates after dyeing with photochromic dye **2** clearly shows the nature of matrix dependence on the photochromic colour build up. Finally, the calculated results indicate that the dye-fibre interactions are also highly influenced with the introduction of two different types of dyes (such as, **1** as a photochromic disperse dye and **2** as a water-soluble photochromic disperse dye) for the dyeing of nylon substrate. As a result there is a variation on the nature of photochromic colour build up which can be one of the reasons for the variation of the level of the chemical affinity of these two dyes for the dyes two pieces of nylon substrates (where, N2 was dyed with **2**, and N1 was dyed with **1**). In addition, due to the change in chemical affinity the nature of dye-uptakes is also highly influenced which may lead to variation in the amount of dye adsorbed by these two dyed nylon samples (N2 and N1) and hence the variation in photochromic colour build up. This observation is strongly supported from the calculated electronic properties of these two dyes which are very briefly presented in this paper.

4. CONCLUSIONS

The nature of photochromic colour build of two different types of spirooxazine based photochromic dyes have been analysed in terms of their behaviours on dyed substrates and also by studying their electronic properties obtained from semi-empirical approach on these two dyes. The observed behaviour of different level of photochromic colour build up determined by specifically developed colour measurement technique have been complemented and to some extend confirms with the results obtained from the semi-empirical study. A further in depth analysis with a range of different classes of photochromic dyes on different substrates at variable conditions will focus on a range of additional important features for detailed analysis which will be published elsewhere in near future.

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