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Theoretical Analysis of the Light Fastness of Reactive Dyes on Cellulose

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Abstract

Five selected reactive dyes were used to perform theoretical calculations of photochemical reactivity indicators in electro-(S^E) and nucleophilic reactions (S^N). The study utilised reactive dyes in which the reactive group is cyanuric chloride, but which differ in their chromophore structure. They belong to the groups of monoazo, disazo and anthraquinone dyes. The influence of changes in these indicators after the formation of the dye-cellulose covalent bond on their light fastness was analyzed. Using the PM3 limit molecular orbital method (MO), the electron density distribution was calculated for dyes in the highest occupied orbital (HOMO) and the lowest unoccupied (LUMO) in the singlet state. These values reflect the tendency towards an electrophilic reaction with a singlet oxygen atom $^1O_2$ or a nucleophilic reaction with the superoxide radical anion $O_2^{\bullet -}$ on atoms in the dye molecule. Reactivity indicators as super delocalization (S^E, S^N) and electron density distribution in the ground and excited states were calculated. The values of the super delocalization coefficients indicate the activity of sites in the molecules in the oxidation reaction, the resistance of these dyes to photo-oxidation and their influence on the durability of chemical bonds with the cellulose. It was found that the formation of bonds with the cellulose slightly affects the resistance in the electrophilic oxidation reaction, but this effect is significant in the nucleophilic reaction.

Keywords

Cellulose, Lightfastness, Reactive Azo and Anthraquinone Dyes, Photochemical Oxidation, PM3 Method, Electrophilic and Nucleophilic Reaction, HOMO and LUMO

1. Introduction

Light fastness of dyed cellulose is one of the most essential features of finished

textiles goods. The phenomenon of fading is complex, and many factors, such as the binding of the dye to the cellulose, the chemical structure of the dye, radiation quality, temperature, and humidity, influence it. Dyes of larger sizes usually take longer to initiate fading: it is inversely proportional to the radius of the dye particle due to the chemical layer effect [1]. A covalent bond with the cellulose ensures the coplanarity of the dye molecules. For greater lightfastness, the dye must have a stable aromatic structure and a minimum number of double bonds or reactive substituents. Electron-donating substituents, e.g. −OH, $-NH_2$, etc., accelerate, while electron-accepting groups, e.g., Cl and Br, retard the fading [2]. The total exposure time is also an important parameter; a short exposure gives the dyed textiles enough time to release the energy needed to return to their initial state. The dye molecule interacting with cellulose exhibits ***p***- and ***n***-type semi conductivity, and their reaction time should be short; higher activation energy for foto-conduction favours higher light fastness [3].

When the reactive dye is in monomolecular form and in interaction with cellulose, the light fastness is expected to be identical to that of the dye molecule itself. However, several publications contradict this view [4]-[7]. It was found that reactive dyes bound by a covalent bond show higher lightfastness than, for example, hydrolyzed forms of dyes. This suggests that the covalent bond between the dye and the cellulose facilitates the transfer of energy from the excited state of the dye molecule to the cellulose macromolecule, changing the rate of dye photodegradation [6]. Other studies have concluded that the nature of the dye-cellulose bond (covalent or adsorption) has negligible effect on light fastness [8]. Such different conclusions may result from other research methods. Some tests were performed on a film through which radiation with the dye's wavelength λ_{max} passed while the dyed fabrics were analyzed visually. In many cases, the covalent bond between cellulose (cotton) and reactive dyes is believed to increase the dyes' light fastness. However, his conclusion still requires additional research [9] [10]. Research on new chemical structures for dyes requires their synthesis, application to a specific material and testing, which is time- and cost-consuming. The results of theoretical calculations carried out for such structures can help reduce the time to evaluate lightfastness without synthesizing and dyeing. In the group of reactive dyes for dyeing cellulose, the most used are symmetric trichloro-triazine derivatives, which react according to the mechanism of nucleophilic substitution. For this reason, five mono-chlorotriazine derivatives reactive dyes with different chromophores were selected for testing.

2. Calculation Methodology

The structures of selected reactive dye molecules and the cellulose molecule model (**Cell**) were optimized using the semi-empirical quantum-chemical method PM3 [11] with complete optimization of all bond lengths, angles between them and torsion angles HyperChem v.8.0.6, Hyper-Cube Inc).

Calculations were made for dyes and for the cellulose fibre model (**Cell**) the

optimized structures in the ground state using the molecular mechanics method [MM+, RMS gradient 0.02 kcal·mol^{-1}·Å^{-1} for the dyes-**Cell** system ([MM+, RMS gradient 0.03 kcal·mol^{-1}·Å^{-1}). After obtaining structure optymised in the ground state by the MM+, the geometry of the molecule was completely optymised by molecular dynamics (MD, runtime 1ps, step size 0.001 ps, simulation temperature 300 K). Finally, the Hartree-Fock Hamiltonian (UMF) was used to calculated configuration interaction (CI) in the gas phase at 25˚C. Next MD and PM3 calculations were performed 3 to 5 times until the lowest standard enthalpy of formation H_f (kcal·mol^{-1}) was constant (0.02 kcal·mol^{-1} gradient). Singlet ground state energies were calculated for the three electrons in HOMO and LUMO states. The λ_{max} with an optimised design of the dyes was calculated using the ZINDO/S method. Calculations using the molecular orbital method (MO) were performed in the gas phase. Standard enthalpies of formation and energies of the HOMO and LUMO states for all dyes were calculated using the PM3 method. This study focused on calculating the possible sites of attack by an oxidizing agent in an electrophilic or nucleophilic reaction in dye molecules. In this work, calculations of the electron density of orbitals in the lowest ground HOMO level and the excited LUMO state of the dye were performed. Frontier's molecular orbital theory suggests that the high electron density region in the dye's HOMO is the site of electrophilic attack by the singlet oxygen $^1O_2$. An area with high electron density in LUMO is where the nucleophilic attack with the superoxide anion radical $O_2^{\bullet -}$ takes place [12].

It is assumed that the attack of an electrophilic agent occurs when the energy difference ΔE between the LUMO of singlet oxygen and the HOMO of the dye is less than 6 eV [13]. The reactivity of carbon atoms in a dye molecule is measured by superdelocalisation coefficients: S^E for electrophilic reactions and S^N for nucleophilic reactions. The values of ΣS^E and ΣS^N illustrate changes in the reactivity of selected atoms before and after they are covalently bonded to a cellulose fibre via cyanuric chloride. ΣE denotes the energy difference between the excited LUMO state and the ground HOMO state, and corresponds to the wavelength of the absorbed visible light, calculated using the ZINDO/S method. The relative tendency of compounds to electrophilic or nucleophilic attack as $S^{E(N)}$ super delocalization is calculated according to formula (1):

$$S_r^{E(N)} = \frac{f_r^{E(N)}}{E_{HOMO(LUMO)}}(-a) \quad (1)$$

where $f_r^{E(N)}$ is a measure of the ground/excited state electron density on atom *r*, and *a* is multiplied to make it dimensionless (−1 eV), which allows comparison of the reactivity of corresponding atoms in different molecules [14]-[17].

The higher these values are, the greater the likelihood of reaction with photodegradable fragments or atoms of the dye molecule by reactive oxygen species (ROS).

3. Results and Discussion

To carry out the calculations, five reactive dyes were used: two monoazo dyes

(derivatives of H acid), 1 diazo dye and 2 anthraquinone derivatives. As a model of the cellulose molecule, a molecule consisting of 3 parts of glucopyranose $(Glu)_3$ = **Cell** was used. First, the structure of each dye molecule was optimized using the molecular mechanics method (MM+), followed by the quantum-chemical method PM3. The structure of the **Cell** was similarly optimized. Such optimized molecules were connected by a covalent bond, and their geometric structure was additionally optimized using the PM3 method (RMS gradient 0.04 kcal·mol^{-1}). Quantum-chemical calculations are carried out in the gas phase to eliminate the influence of the solvent (and also the fibre) on the colour and, consequently, on the performance properties of the dyes. The calculations also omit $-SO_3H$ groups, which only affect the water solubility of the dyes; no effect of these groups on lightfastness has been observed. During the calculations, changes in reactivity coefficients were analysed—super delocalization in the reaction of electrophilic oxidation of S^E with singlet oxygen $^1O_2$ and nucleophilic S^N with the use of $O_2^{\bullet-}$ superoxide anion radical. The higher the S^E or S^N values, the faster the reaction on the analyzed atom is. The reactivity and changes for unbound dyes and those chemically bound to the **Cell** molecule were compared.

Changes in the electron density on the oxygen atom in the binding of the dye to the dyed cellulose with reactive chlorotriazine dyes lead to the formation of covalent bonds as a result of the S_{N2} nucleophilic reaction between the ionized hydroxyl group (particularly located at the C_6 carbon in the methylol group—CH_2OH) in the glucopyranose residue with the reactive atom of the dye center, which is the polarized N-Cl bond in chlorotriazine. The formation of a covalent bond between the reactive dye and the **Cell** (Figure 1) causes changes in the electron density in the cellulose residue and reactive dye.

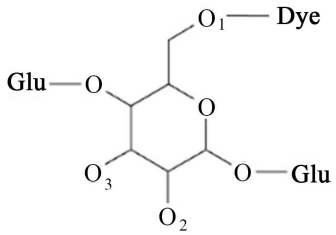

Figure 1. Model of the "**Dye-Cell**" adopted for research and calculations.

In the reaction with the reactive dye, the hydroxyl group of the methylol substituent (O_1) is reactive. The calculation results are presented in Table 1.

Table 1. Changes in the electron density f^H on the O1 oxygen atom after binding the tested reactive dyes with **Cell**.

Dye	RR12 + Cell	RR45 + Cell	RBr1 + Cell	RB2 + Cell	RB5 + Cell
f^H(O1)	−0.142	−0.138	−0.143	−0.148	−0.136
Δf^H(O1)	58.7	59.9	58.4	57.0	60.5

$f^H_{(Cell)} = -0.344$; $\Delta f^H_{(O1)}$ (%) = $(f^H_{(Cell)} - f^H_{(O1)})/f^H_{(Cell)}$.

These changes concern only the oxygen atom O_1, which forms a covalent bond with the cyanuric chloride. All dyes, after forming a covalent bond with the **Cell**, cause a decrease in the electron density on the oxygen atom O_1, and this change is over 50% about the initial value $f^{H}_{(Cell)} = -0.344$ (Table 1). The highest change occurs for the **RB5** dye and the smallest for **RB2**. On O_2 and O_2 atoms in the glucopyranose ring, these changes are no greater than 1.7 ÷ 2.6%.

3.1. Calculations for Reactive Red 12 [18]

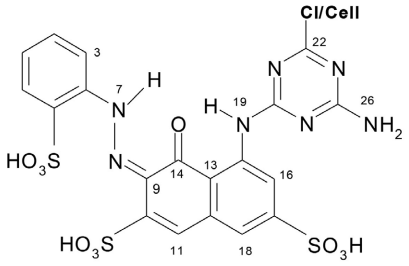

Figure 2. Model **RR12 + Cell** adopted for research and calculation.

This dye exists in the hydrazone form (Figure 2). The formation of a dye bond with the **Cell** causes a hypochromic effect of approximately 5 nm (ZINDO/S), which results from changes in the energy of the LUMO level (Table 2).

Table 2. Energy and color changes in HOMO and LUMO of **RR12** and **RR12 + Cell.**

	RR12		**RR12 + Cell**	
	λ_{max}[nm]	f	λ_{max}[nm]	f
PM3	404.5	0.815	395.2	0.733
ZINDO/S	410.7	0.692	406.0	0.644
ΔE	6.8194		6.9274	

$\Delta E = E_{HOMO} - E_{LUMO}$ kcal·mol^{-1}.

The most susceptible to photooxidation (S^E) in **RR12** (Table 3 and Figure 3) are the carbon atoms C9 (0.0328), C13 (0.0235) and C16 (0.0230). As a result of forming a bond with **Cell**, the reactivity of the atom C16 (0.0230 → 0.0136) changes significantly, *i.e.*, it decreases by 41.0%. In other cases, they are much smaller and amount to C9 3.87% and C13 8.08%.

Table 3. Theoretical values electron densities (f^E, f^N) and reactivity (S^E, S^N) on the most reactive atoms in the **RR12** dye and in **RR12 + Cell** after formation of the covalent bond.

RR12			**RR12 + Cell**		
Atom	f^E	S^E		f^E	S^E
E_{HOMO} = −8.2496 kcal·mol^{-1}			E_{HOMO} = −8.4034 kcal·mol^{-1}		
9	−0.2705	0.0328	9	−0.2649	0.0315
11	−0.1438	0.0174	11	−0.1415	0.0168
13	−0.1937	0.0235	13	−0.1819	0.0216

Continued

16	−0.1897	0.0230	18	−0.1280	0.0152
$\Sigma(S^E/f^E)$	−0.7977	0.0967	$\Sigma(S^E/f^E)$	−0.7163	0.0852
				10.20%	**11.86%**
	RR12			**RR12 + Cell***	
Atom	f^N	S^N		f^N	S^N
E_{LUMO} = −1.4302 kcal·mol^{-1}			E_{LUMO} = −1.4760 kcal·mol^{-1}		
7	0.4030	0.2818	7	0.4020	0.2724
14	0.2896	0.2025	14	0.2885	0.1955
19	0.2108	0.1474	19	0.1512	0.1024
			22	*0.2201*	*0.1491*
26	0.15073	0.1054	26	0.1554	0.1053
$\Sigma(S^N/f^N)$	1.0541	0.7371	$\Sigma(S^N/f^N)$	0.9971	0.6755
				5.41%	**8.36%**

*excluding C22.

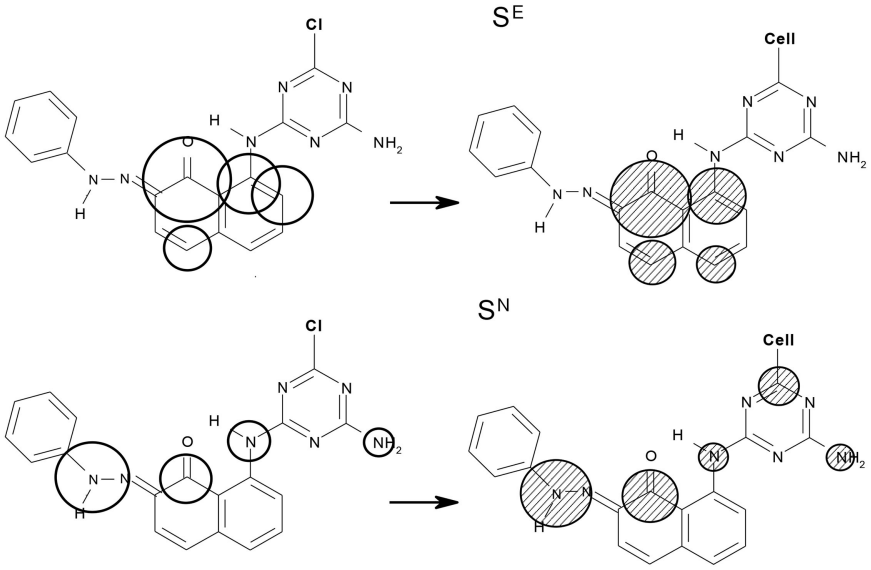

Figure 3. An example of a graphical presentation of changes in the most reactive atoms of RR12, unbound (open cycle) and bound to Cell (patterned cycle). The size of the circle is proportional to the value of the super delocalization coefficient in the reaction of electrophilic S^E or nucleophilic oxidation of S^N.

The sum of the super additivity indicators ΣS^E for the reactive carbon atoms is 11.86% lower compared to the atoms in reactive dye not bonded to the **Cell** (**Table 3**). In the case of **RR12** dye, forming a bond with the **Cell** should increase lightfastness.

In the nucleophilic photooxidation reaction of S^N using the superoxide anion radical $O_2^{\bullet-}$, the dye binding to the **Cell** increases the resistance to photooxidation, the lightfastness should be better. The total change in the reactivity ΣS^N of the **RR12 + Cell** bound dye compared to the unbound dye is 8.36%. (0.7371 →

0.6755). The most significant change in the value of the delocalization coefficient occurs at the carbon atom C19 and amounts to 30.52%. The most reactive atoms in the S^N reaction are C7 (0.2724) and C14 (0.1955).

Also noteworthy is the high reactivity at the carbon atom C22 (0.1491), which forms a covalent bond between the chlorotriazine molecule and **Cell**. In the case of C7 and C14 atoms, the reaction should lead to a change or disappearance of color because of changes in the dye's chromophore system, the change at the C22 atom would be responsible for the bond brake between the dye and the cellulose (Table 3 and Table 4).

Table 4. Changes in the super delocalization coefficient S^E in the cyanuric chloride ring after binding **RR12** dye with **Cell**.

	RR12-Cy-Cl	RR12-Cy-Cell
ΣS^E	0.0972	0.1049
Δ [%]		+7.34

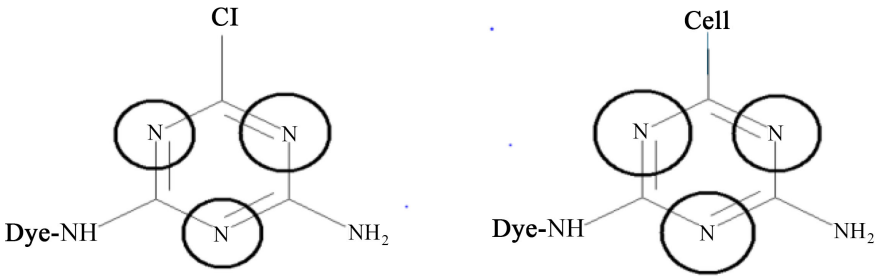

Figure 4. Graphical illustration of the changes in the super delocalization coefficient S^E in cyanuric chloride ring after binding the **RR12** dye to **Cell**.

Table 4 and Figure 4 presents the changes in the super delocalization coefficient S^E in cyanuric chloride ring after binding of the **RR12** dye to **Cell.**

3.2. Calculations for Reactive Red 45 [19]

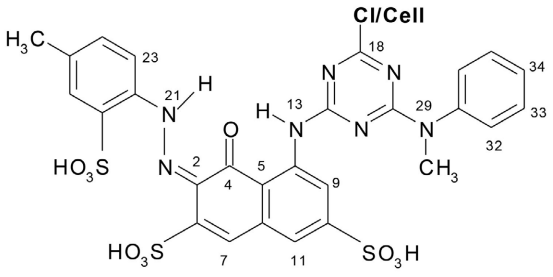

Figure 5. Model **RR45 + Cell** adopted for research and calculation.

RR45 dye (Figure 5) is a derivative of H acid and is available in the hydrazone form. Its bonding with the **Cell** causes the hypochromic effect by 11.2 nm (ZINDO/S) (Table 5).

Table 5. Energy and color changes in HOMO and LUMO of **RR45** and **RR45 + Cell**.

	RR45		**RR45 + Cell**	
	λ_{max}[nm]	f	λ_{max}[nm]	f
PM3	397.3	0.727	396.0	0.707
ZINDO/S	419.9	0.676	408.7	0.638
ΔE	6.8834		6.9060	

This is due to the energy reduction of the 1st excited state of LUMO from -1.4083 kcal·mol^{-1} to −1.4357 kcal·mol^{-1} ($\Delta E_{HOMO\text{-}LUMO}$ = 6.8407 kcal·mol^{-1}).

Table 6. Theoretical values electron densities (f^E, f^N) and reactivity (S^E, S^N) on selected atoms in the **RR45** dye and **RR45 + Cell** after formation of the covalent bond.

RR45			**RR45 + Cell***		
Atom	f^E	S^E		f^E	S^E
E_{HOMO} = −8.2636 kcal·mol^{-1}			E_{HOMO} = −8.2764 kcal·mol^{-1}		
2	−0.2739	0.0332	2	−0.2743	0.0331
5	−0.1840	0.0223	5	−0.1906	0.0230
7	−0.1434	0.0174	7	−0.1466	0.0177
11	−0.1303	0.0158	9	−0.1404	0.0170
$\Sigma(S^E/f^E)$	−0.7316	0.0885	$\Sigma(S^E/f^E)$	−0.7519	0.0908
				−2.77%	**−2.60%**
RR45			**RR45 + Cell***		
Atom	f^N	S^N		f^N	S^N
E_{LUMO} = −1.4083 kcal·mol^{-1}			E_{LUMO} = −1.4357 kcal·mol^{-1}		
4	0.2879	0.2044	4	0.2896	0.2016
13	0.1568	0.1114	13	0.1680	0.1170
			18	0.2203	0.1535
N21	0.4140	0.2940	21	0.4127	0.2874
29	0.1440	0.1022	29	0.1514	0.1054
$\Sigma(S^N/f^N)$	1.0027	0.7120	$\Sigma(S^N/f^N)$	1.0215	0.7115
				−1.89**%**	**0.08%**

*excluding C18.

RR45 dye has an additional methyl group at the N29 nitrogen atom. The C2 atom (S^E = 0.0331) and C5 (S^E = 0.0223) have the highest reactivity in the electrophilic photooxidation reaction. Binding to **Cell** changes these values slightly. The most notable change is observed at C9 carbon atom, by 20.36%. Binding to the **Cell** means this dye should be more susceptible to reaction with singlet oxygen $^1O_2$. The electrophilic S^E photooxidation reaction should occur at the C2 (0.0332) carbon atom and then at the C5 (0.0223) atom. The most notable change in the S^E

value is observed at the C9 carbon atom, by 15.49%. Changes in the S^E value on the remaining atoms susceptible to attack molecule oxygen $^1O_2$ are insignificant and amount to 2% - 3% (Table 6). Finally binding **RR45** dye to the **Cell** causes its lightfastness to decrease in the electrophilic reaction by 2.60% (ΣS^E 0.0885 → 0.0908).

Greater changes are observed in the nucleophilic photooxidation of S^N using the superoxide anion radical $O_2^{\bullet -}$, while N21 (0.2940) and C4 (0.2044) are the most reactive atoms. This type of reaction can also occur at the C18 (0.1535) carbon atom; the effect should be to break the bond with the cellulose, *i.e.*, reduce the resistance to wet factors. Oxidation at C4, C13 and N21 atoms should destroy the chromophore system and the vanishing of the dye's color. The most extensive changes in the super delocalization coefficient occur on the C13 atom by 5.07%.

In the S^N reaction, dye binding with the **Cell** should cause a slight reduction in the dye's reactivity to photooxidation by 0.07% (ΣS^N), it means that lightfastness should be increased.

Table 7. Changes in the superdelocalization coefficient S^E in the cyanuric chloride ring after bonding **RR45** dye with **Cell.**

	RR45-Cy-Cl	RR45-Cy-Cell
ΣS^E	0.0743	0.0886
Δ [%]		16.14

Forming the bond with the cellulose slightly reduces light resistance and oxidizing agent by 16.14% (Table 7). Like in the case of the dye discussed previously, the reactivity of the C18 carbon atom, which is involved in forming a bond with the cellulose, increases significantly (0.1535). The nucleophilic oxidation reaction should occur for **RR45 + Cell** in the following order:

N21 (0.2874) > C4 (0.2016) > C18 (0.1535)

i.e., the dye **RR45** should first change its color due to changes in the chromophore system (N21, C4 atom), then undergo bond breaking with the **Cell** at the C18 atom in a reaction catalyzed by the $O_2^{\bullet -}$ superoxide radical anion.

3.3. Calculations for Reactive Brown 1 [18]

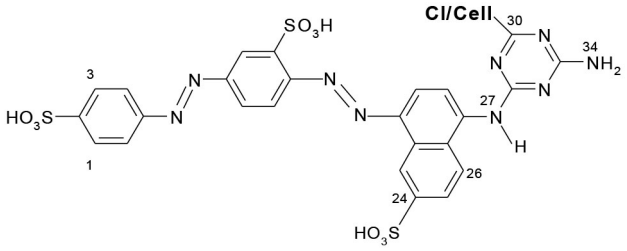

Figure 6. Model **RBr1 + Cell** adopted for research and calculation.

Reactive Brown 1 (Figure 6) is a diazo dye. It occurs only in the azo form and is a derivative of 1-Aminonaphthalene-6-sulfonic acid (Cleve acid-1,6). As a result of

binding to the cellulose, it should exhibit a bathochromic effect of 4.0 nm (Table 8).

Table 8. Energy and color changes in HOMO and LUMO of **RR45** and **RR45 + Cell**.

	RBr1		**RBr1 + Cell**	
	λ_{max}[nm]	f	λ_{max}[nm]	f
PM3	345.8	1.448	357.6	1.245
ZINDO/S	368.4	1.409	372.4	1.402
ΔE	7.2381		7.0545	

$\Delta E = E_{HOMO} - E_{LUMO}$ [kcal·mol^{-1}].

Table 9. Theoretical values electron densities (f^E, f^N) and reactivity (S^E, S^N) on selected atoms in the **RBr1** dye and **RBr1 + Cell** after formation of the covalent bond.

RBr1			**RBr1 + Cell***		
Atom	f^E	S^E		f^E	S^E
E_{HOMO} = −8.5622 kcal·mol^{-1}			E_{HOMO} = −8.2680 kcal·mol^{-1}		
1	−0.1128	0.0132	1	−0.1116	0.0135
3	−0.1087	0.0127	3	−0.1078	0.0130
24	−0.1035	0.0121	24	−0.1030	0.0125
26	−0.1123	0.0131	26	−0.1082	0.0131
$\Sigma(S^E/f^E)$	−0.4374	0.0511	$\Sigma(S^E/f^E)$	−0.4306	0.0521
				1.55%	**−1.96%**
RBr1			**RBr1 + Cell***		
Atom	f^N	S^N		f^N	S^N
E_{LUMO} = −1.3241 kcal·mol^{-1}			E_{LUMO} = −1.2135 kcal·mol^{-1}		
27	0.2950	0.2228	27	0.4089	0.3369
			30	0.2307	0.1901
34	0.1601	0.1209	34	0.1475	0.1215
$\Sigma(S^N/f^N)$	0.4551	0.3437	$\Sigma(S^N/f^N)$	0.5563	0.4585
				22.24%	**−33.40%**

*excluding C30.

RBr1 forming bonds with the **Cell** reduces its resistance in the electrophilic reaction with $^1O_2$ by approximately 1.96% (ΔS^E 0.0511 → 0.0521). Changes in reactivity in selected atoms are slight, up to about 3%. The most reactive atoms should be C1 (0.0135) and C26 (0.0131) (Table 8 and Table 9). These values are almost 2.5 times lower than for monoazo dye molecules. At the same time, the superdelocalisation coefficients ΣSE in the cyanuric chloride ring change as shown in Table 10.

In the nucleophilic reaction, the highest reactivity is characterized by the N27

nitrogen atom (0.3369), higher than that of a dye unbonded to **Cell** by as much as 51.25%. The C30 carbon atom (0.1901) is also characterized by high reactivity. In the S^N reaction, the increase in reactivity is $\Delta S^N = -33.40\%$ for the dye bound to the **Cell**. The calculated values indicate that this dye should have lower lightfastness and wet fastness compared to the previously discussed monoazo dyes.

Table 10. Changes in the super delocalization coefficient S^E in the cyanuric chloride ring after bonding **RBr1** dye with **Cell**.

	RBr1-Cy-Cll	**RBr1-Cy-Cell**
ΣS^E	0.0901	1.1110
Δ [%]		+18.82

This dye should undergo bond breaking due to a reaction with superoxide anion radical $O_2^{\bullet -}$; it has a remarkably high S^N value on the C30 carbon atom, forming a bond with the cellulose. N27 atoms and N34 are not components of the chromophore system of the dye; the dye should be removed by breaking the bond with **Cell**.

3.4. Calculations for Reactive Blue 2 [18]

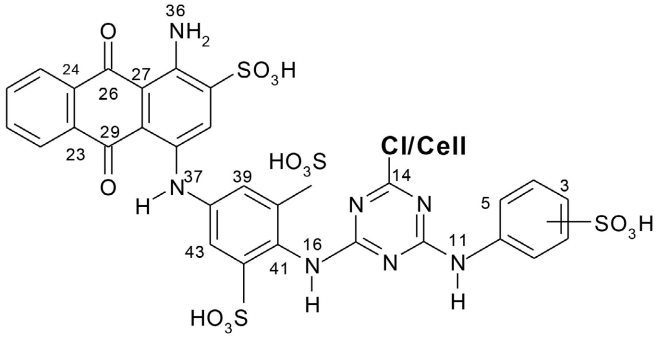

Figure 7. Model **RB2 + Cell** adopted for research and calculation.

Table 11. Energy and color changes in HOMO and LUMO of **RB2** and **RB2 + Cell**.

	RB2		**RB2 + Cell**	
	λ_{max}[nm]	f	λ_{max}[nm]	f
PM3	343.7	0.232	332.1	0.205
ZINDO/S	342.9	0.315	335.1	0.310
ΔE	7.0257		7.2132	

$\Delta E = E_{HOMO} - E_{LUMO}$ [kcal·mol^{-1}].

Cell colored with **RB2** should cause the hypochromic effect of 7.8nm (ZINDO/S) because of a significant reduction in the HOMO energy of the dye in the bound state with **Cell** (Table 11). The formation of a bond with the **Cell** by **RB2** (Figure

7) should reduce its resistance to light in the electrophilic $^1O_2$ reaction by 9.90% (ΔS^E 0.0755 → 0.0687). The most reactive carbon atom is C27 (0.0236), followed by C39 (0.0179). On the remaining atoms, the reactivity changes are insignificant ≤ 3% (Table 12).

Table 12. Theoretical values electron densities (f^E, f^N) and reactivity (S^E, S^N) on selected atoms in the **RB2** dye and **RB2 + Cell** after formation of the covalent bond.

RB2			**RB2 + Cell***		
Atom	f^E	S^E		f^E	S^E
E_{HOMO} = −8.3015 kcal·mol^{-1}			E_{HOMO} = −8.48610 kcal·mol^{-1}		
27	−0.1868	0.0225	27	−0.2003	0.0236
31	−0.1289	0.0155	31	−0.1437	0.0169
39	−0.1304	0.0157	39	−0.1517	0.0179
41	−0.1239	0.0149	43	−0.1450	0.0171
$\Sigma(S^E/f^E)$	−0.5700	0.0687	$\Sigma(S^E/f^E)$	−0.6407	0.0755
				12.40%	**−9.96%**
RB2			**RB2 + Cell***		
Atom	f^N	S^N		f^N	S^N
E_{LUMO} = −1.2757 kcal·mol^{-1}			E_{LUMO} = −1.2729 kcal·mol^{-1}		
11	0.1984	0.1555	11	0.2114	0.1661
			14	*0.2299*	*0.1806*
26	0.3314	0.2598	26	0.3275	0.2573
29	0.3611	0.2830	29	0.3692	0.2901
37	0.2716	0.2129	37	0.2372	0.1863
$\Sigma(S^N/f^N)$	1.1624	0.9111	$\Sigma(S^N/f^N)$	1.1453	0.8998
				1.47%	**1.24%**

*excluding C14.

Calculations show that the cellulose-bound dye in the process of photodegradation occurring according to S^E induces a decrease lightfastness, and according to the S^N mechanism, an increase lightfastness (Table 12).

In the nucleophilic reaction, the reaction center is the C29 carbon atom of the anthraquinone set carbonyl group (S^E = 0.2901). The increase in reactivity is consumed on the C37 atom by 12.46% (0.2129 → 0.1863). The nucleophilic reaction also produces reactivity at the C14 carbon atom (0.1806), forming a covalent compound with the cyanuric chloride.

The course of photo-oxidation transmission should first result in the discoloration of the dye due to changes in its chromophore system, followed by its breaking bond with **Cell** and migration from cellulose, e.g., to the dyeing or washing bath (Table 13). Moreover, in the S^N reaction, the lightfastness of the dye increases by 1.24% after binding to **Cell**, calculated in the values of the super additivity

coefficients ΣS^N.

Table 13. Changes in the super delocalization coefficient S^E in the cyanuric chloride ring after bonding **RB2** dye with **Cell**.

	RB2-Cy-Cl	RB2-Cy-Cell
ΣS^E	0.0922	0.1021
Δ [%]		+9.69

3.5. Calculations for Reactive Blue 5 [18] [20]

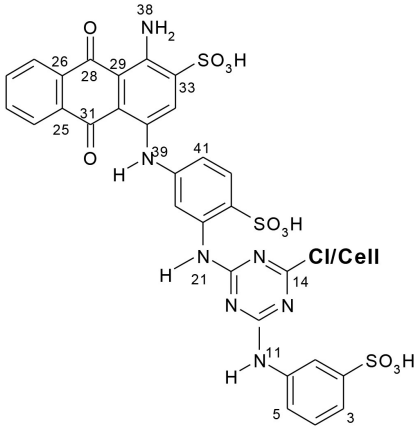

Figure 8. Model **RB5 + Cell** adopted for research and calculation.

RB5 dye (Figure 8) is an **RB2** isomer in which the cyanuric chloride residue is attached to the anthraquinone dye via m-phenylenediamine (**RB2** → p-phenylene-diamine). Binding to the **Cell** causes a small bathochromic effect of 2.0 nm. It results from increasing the energy of the HOMO ground state by 0.0337 kcal·mol^{-1} and LUMO by 0.0141 kcal·mol^{-1} ($\Delta E_{HOMO\text{-}LUMO}$ = 7.0915 kcal·mol^{-1}) (Table 14).

Table 14. Energy and color changes in HOMO and LUMO of **RB5** and **RB5 + Cell**.

	RB5		RB5 + Cell	
	λ_{max}[nm]	f	λ_{max}[nm]	f
PM3	337.0	0.178	342.5	0.200
ZINDO/S	336.4	0.271	338.4	0.273
ΔE	7.1112		7.0915	

RB5 forming a bond with **Cell** should reduce lightfastness by 1.28% compared to the dye not bound in the electrophilic reaction with $^1O_2$. The most notable change is observed at the C41 carbon atom by 5.20%.

In the nucleophilic reaction with superoxide radical anion $O_2^{\bullet -}$, the formation of a bond with **Cell** causes a slight deterioration in lightfastness by 15.88% (Table 15) and is subject to change superdelocalisation coefficient ΣS^E in cyjanuric ring (Table 16). The highest reactivity is characterized by C31 carbon atom (0.2851)

and C28 (0.2849). The C14 atom (0.1846), which forms a bond between the dye and the Cell, is also highly reactive. However, it is lower than the reactivity of the anthraquinone residue.

Table 15. Theoretical values electron densities (f^E, f^N) and reactivity (S^E, S^N) on selected atoms in the **RB5** dye and **RB5 + Cell** after formation of the covalent bond.

RB5			**RB5 + Cell***		
Atom	f^E	S^E		f^E	S^E
E_{HOMO} = −8.3429 kcal·mol^{-1}			E_{HOMO} = −8.3092 kcal·mol^{-1}		
5	−0.1214			−0.1247	0.0150
29	−0.1780	0.0213	29	−0.1750	0.0211
41	−0.1628	0.0195	41	−0.1538	0.0185
45	−0.1253	0.0150	45	−0.1240	0.0149
$\Sigma(S^E/f^E)$	−0.5875	0.0704	$\Sigma(S^E/f^E)$	−0.5775	0.0695
				1.70%	**1.28%**
RB5			**RB5 + Cell***		
Atom	f^N	S^N		f^N	S^N
E_{LUMO} = −1.2317 kcal·mol^{-1}			E_{LUMO} = −1.2176 kcal·mol^{-1}		
11	0.1965	−0.1595	11	0.2008	−0.1649
			14	0.2248	−0.1846
28	0.3509	−0.2849	21	0.1689	−0.1387
31	0.3511	−0.2851	28	0.3402	−0.2794
39	0.2908	−0.2361	39	0.2790	−0.2292
$\Sigma(S^N/f^N)$	1.1892	0.9655	$\Sigma(S^N/f^N)$	0.9889	0.8122
				16.84%	**15.88%**

*excluding C14.

Table 16. Changes in the super delocalization coefficient S^E in the cyanuric chloride ring after bonding **RB5** dye with **Cell**.

	RB5-Cy-Cl	**RB5-Cy-Cell**
ΣS^E	0.0909	0.1065
Δ [%]		+14.64

3.6. Influence of S^E and S^N Type Photodegradation on Light Fastness

Computer calculations showed that analyzed dyes and their combinations with **Cell** behave differently under conditions favoring the electrophilic/nucleophilic

reaction using active oxygen compounds, $^1O_2$ and $O_2^{\bullet -}$, respectively and proceed in accordance with the reactions considered by other authors [21]-[26]:

$$dye \xrightarrow{light} dye^* + {}^3O_2 \xrightarrow{electron\ transfer} dye^{\bullet +} + O_2^{\bullet -}$$

Although many modelling studies have shown that singlet oxygen $^1O_2$ is very reactive in dyes [21] [22], its significance is unclear. Recent work suggests that its role in the photobleaching of azo dyes is relatively small [23] [24].

It has also been shown that the quenching of the excited states of dyes by oxygen leads to the formation of the superoxide anion $O_2^{\bullet -}$ and the destruction of the dye [25]. The formed superoxide anion radical can further react, destroying subsequent dye molecules [26].

The direction and course of the reaction is clearly related to changes in the electron density on the atoms of dye molecules and their superdelocalization in the HOMO and LUMO states. An increase in the reactivity of the molecule with the active form of oxygen means an increase in the photodegradation of the dye, which is equivalent to a decrease in lightfastness. Based on the results, the dyes can be ranked from most to least resistant to photodegradation by electrophilic S^E oxidation reaction as follows:

RR12 (+11.89) > **RB5** (+1.28) > **RBr1** (−1.96) > **RR45** (−2.60) > **RB2** (−9.90)

In the nucleophilic reaction of S^N using the anion-radical $O_2^{\bullet -}$, the formation of bonds with the **Cell** causes changes in the lightfastness as follows:

RB5 (+15.88) > **RR12** (+8.35) > **RB2** (+1.24) > **RR45** (+0.07) > **RBr1** (−33.40)

It can be concluded that more sensitive to superoxide anion radical $O_2^{\bullet -}$ oxidation in the S^N reaction are the bonds of anthraquinone derivatives and the diazo dye, while the bonds of monoazo dyes are more stable.

4. Summary

The performed calculations of the lightfastness for five reactive dyes, cyanuric chloride derivatives, not bonded and covalently bonded to cellulose. These dyes belong to the group of monoazo and diazo dyes, and anthraquinones. As cellulose molecule model **Cell** = $(Glu)_3$ has been used.

Using the PM3 method, the changes in the reactivity indicators for unbound reactive dyes and in the **Cell + Dye** model were calculated. Calculations were performed for the electrophilic photooxidation reaction of S^E with oxygen in the singlet state $^1O_2$ and the nucleophilic reaction of S^N with the anion radical $O_2^{\bullet -}$.

The calculations S^E indices indicate that bond formation with the **Cell** should slightly reduce light resistance compared to unbound dyes. The performed reactivity comparison for the most reactive atoms in the molecules, determined the sum of the values of the super delocalization coefficients ΣS^E.

A similar method was used to calculate the S^N indices in the photooxidation reaction according to the nucleophilic mechanism using the $O_2^{\bullet -}$ anion radical.

An increase in the reactivity of the molecule with the active form of oxygen

means an increase in the photodegradation of the dye, which is equivalent to a decrease in lightfastness. The calculations indicate that bond formation with the **Cell** should slightly reduce lightfastness comparing to unbound dyes.

The calculations indicate that the PM3 method can predict the sites of electrophilic and nucleophilic attack of the oxygen molecule on the reactive dye bound with **Cell** by a covalent bond. This method has not been used before for this type of calculations and allows the analysis of dyes resistance to light to be extended with numerical methods. They can complement the comparative analysis based on the grey scale used in textile practice.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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