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Substantivity and spatial structure of soluble polycyclic dyes for dyeing cellulose fibres

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Abstract

Several polycyclic dyes, derivatives of imidazole and imide derivatives of a perylenetetracarboxylic-3,4,9,10 anhydride have been synthesized. Dyes obtained by adding sulpho groups to original dye molecules were used to dye cellulose fibres in the same way as with direct dyes. The resultant dyeings have a good fastness to washing, abrasion and light. Probable sites of a substitution of sulpho groups in dyes were determined by calculating a total energy of molecules by means of a semiempirical molecular orbital AM1 method and also a reason of a substantivity of imidazole dyes was explained.

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Keywords: Direct dyes; AM1 method; Soluble polycyclic dyes; Perylenetetracarboxylic-3,4,9,10 anhydride

1. Introduction

One of conditions for obtaining dyes high substantivity to cellulose fibres is their flat and linear structure. The most numerous dyes are azo dyes due to their good cost efficiency, easy synthesis and simple application procedures as well as their good performance properties. However, their fastness to light is not always at the highest level, which may result in a formation of harmful products of chemical decomposition. For instance, benzidine dyes, which are very good in the terms of fastness, reproduce the carcinogenic benzidine as a result of photochemical decomposition and this one belongs to a harmfulness group MAK III A1.

The non-azo organic polycyclic pigments are the dyes of the highest lightfastness, but unfortunately they cannot be used to dye natural fibres with a dyebath method. Their high fastnesses are the result of intermolecular hydrogen bonds or van der Waals forces, i.e. the same interactions which are responsible for the affinity of direct dyes to cellulose fibres. In our work we have studied a possible transformation of some pigments into direct dyes by introducing sulpho groups to their molecules, thus the aim of our studies was to impart a solubility to perylene pigments and to use them as soluble direct dyes for dyeing cellulose fibres.

The derivatives of perylenetetracarboxylic-3,4,9,10 acid are known as pigments suitable in many applications [1,2]. They are used as vat dyes, pigments, fluorescent dyes for solar collectors and also as absorbers of IR radiation in a laser technique for producing masking clothes. Their fluorescence yield is almost of 100% and they are stable during 4 h of heating at a temperature of 220 °C in a quinoline solution. It is quite difficult to prepare pure derivatives, especially in special applications, due to their insolubility and therefore in some aspects of their future uses the great emphasis is put on foreseeing their properties by means of quantum and chemical computational methods, e.g., PPP-MO [3], INDO/S [4,5], AM1 [4,5].

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With azo dyes, as a result of their decomposition, harmful aromatic amines can be produced. The use of polycyclic pigments and vat dyes following an appropriate modification of their structure for dyebath dyeing can be an alternative solution. Pigments and vat dyes are usually prepared in a complex procedure, but their use is more environmentally friendly than that of the azo dyes. There are some defects of application of these dyes such as a complicated dyeing of woven fabrics, considerable consumption of energy and fabric stiffening in a process with printed designs make it desirable to impart solubility to potentially allow their use in simple dyebath method of dyeing.

2. Experimental

Diimides and diimidazoles of perylenetetracarboxylic-3,4,9,10 anhydride were prepared as described in the literature [2,6]. A sulphonation of the obtained pigments was carried out according to the procedure described previously [6]. Sulpho groups were determined by titration with a hyamine solution [7].

Calculations of spatial structure of dyes were performed by the AM1 method (Hyperchem v. 5.02, Hypercube Inc.) according to the procedure described in the literature [8].

A spectrophotometric analysis of aqueous solutions of dyes of concentrations 5.75×10^{-5}–1.15×10^{-4} M/dm^3 were carried out using a SPECORD M40 apparatus (Zeiss Jena).

3. Dyeing

Conventional bleached and mercerised woven cotton fabric was used. The dyeings were performed in a Roaches–Rotec apparatus with a temperature accuracy of ±1 °C. The dyeing process was carried out in a dyebath of a 30:1 liquor ratio, containing 0.025 g of 100% dye (1% of dyeing) in 10% Na_2SO_4 solution. The dyeing method is shown in Fig. 1.

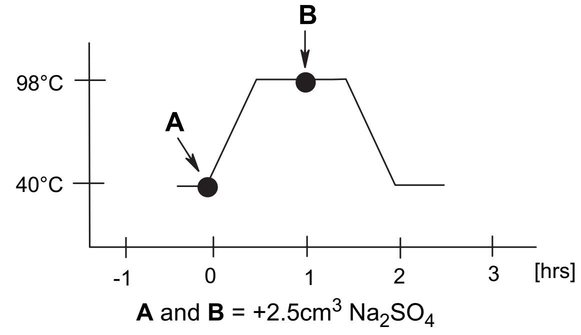


Fig. 1. Dyeing method.

At the end of dyeing, the dyed sample was removed, rinsed in the cold water for 10 min and then dried in the open air. The degree of the dye exhaustion W from the dyebath was determined by the spectrophotometric method, using the following relationship:

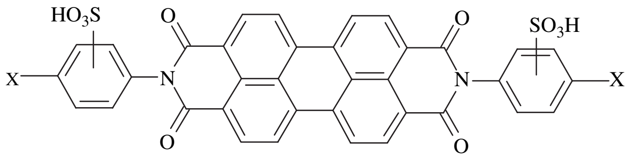
$$W = [(A_1 - A_2)/A_1] \times 100\%$$

where A_1, A_2 are the dye absorbance in the solution before and after dyeing, respectively.

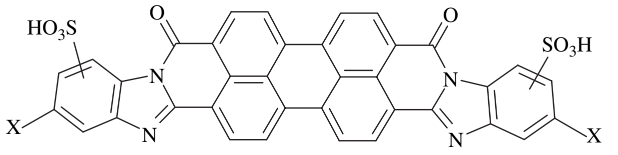
The dyed fabrics were evaluated by means of a standard procedure: fastness of the 1/1 standard depth according to ISO 105-E01, fastness to washing according to ISO 105-C01. Fastness to light of the dyed fabric was performed according to ISO 105-B02, by use of a Xenotest 150S (Heraus–Hanau) apparatus. A colour change was estimated against the blue wool standard scale 1 (poor)–8 (excellent).

4. Results

Water-soluble imide dyes **B1**–**B3** and imidazole dyes **B4**–**B6** with sulpho group content about two were prepared by direct sulphonation.



B1 - B3



B4 - B6

X = H, CH_3, Cl

Fastnesses of the dyes **B1**–**B6** were tested and the results are given in the Table 1.

The obtained dyes have the very good fastnesses, especially the high fastness to light.

Table 1
Fastnesses of dyes **B1**–**B6**

Dye	Washing			Staining		Light
	Cell	Colour change	Wool	Dry	Wet	
B1	5	5	5	5	4–5	7–8
B2	5	5	5	5	5	7–8
B3	5	5	5	5	5	7–8
B4	4	4	5	5	4	6
B5	4–5	4–5	5	5	4	6
B6	4–5	4–5	5	5	4	6

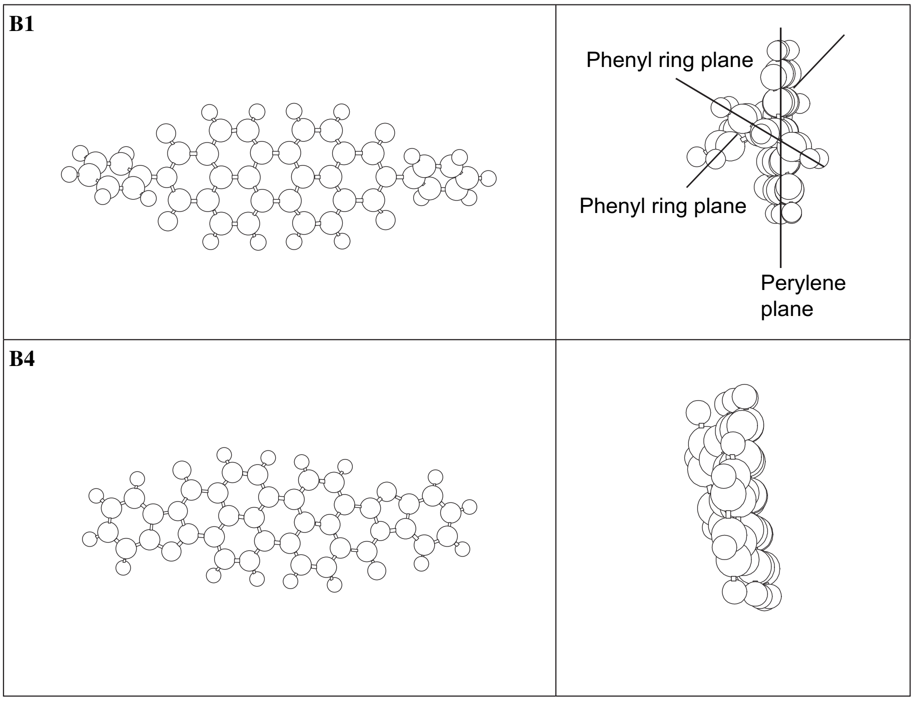


Fig. 2. Spatial structures of dyes **B1** and **B4**.

The dyes **B1**–**B3** coloured cellulose fibres to shades of red and of reddish blue. High differences in the degrees of dye exhaustion from the dyebath indicate that there is a relationship between the substantivity and the structure of the dye. This issue can be explained, similarly as the substitution site of sulpho groups, by means of quantum and chemical calculations with the AM1 method. The optimisation procedure of geometric structure by the AM1 method and the molecular dynamics were used for calculating the total energy [8,9].

5. Spatial structure of dyes

The performed calculations show that the molecules of dyes **B1**–**B3** are not flat. The phenylimide group (**B1**–**B3**) is deflected beyond the perylene ring plane. The imidazole derivatives (**B4**–**B6**), due to the obstruction of heterocyclic ring rotation, have a near-flat structure (Fig. 2). This is confirmed by the results of the determination of the dye exhaustion degree. The decreased values of *W* for **B6** are the probable result of the substituent size, which makes the access of the dye to the cellulose molecule surface difficult and also weakens the interaction of the van der Waals forces (dispersion forces). This effect could be observed already in the methyl derivatives (**B5**), in which case the exhaustion degree was decreased of about 10% as compared to the dye with no additional substituents.

Results of determination of the number of sulpho groups show that about two sulpho groups can be introduced to the pigment molecule, but the substitution site is unknown. The most probable thing is that these groups are in the phenyl ring, as the ring of perylene anhydride cannot be sulphonated. The substitution site can be determined only by quantum and chemical calculations and by estimating the total energy of the sulphonated dye molecules (Fig. 3). Such calculations

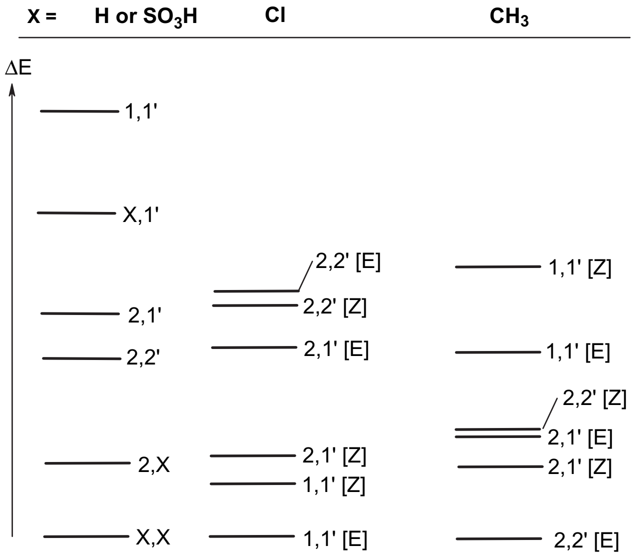


Fig. 3. Graphical dependence of the dye molecule energy on the type of substituent and the substitution site of sulpho groups.

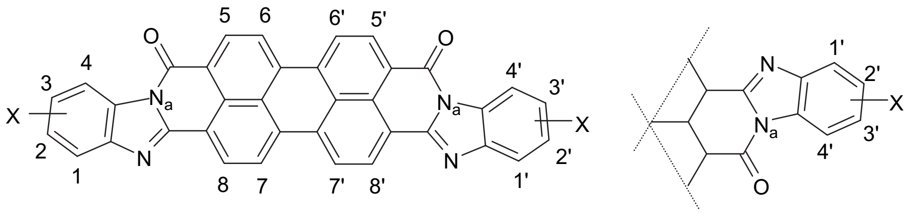
also allow to explain the cause of the low substantivity of sulphonated imide derivatives to cellulose fibres. Imide rings of an imide molecule are located in planes which are almost perpendicular to the perylene ring and that is why one of the most important conditions of the dye substantivity to cellulose fibres is not good enough.

The calculation of geometric structure was carried out for all the possible sites of sulpho group substitution, taking into account the possibility of arrangement of these groups in *cis* positions (at the same side of perylene skeleton – isomer *Z*) and *trans* (at the opposite sides of perylene skeleton – isomer *E*) to each other. This allows one to foresee the substitution site of $-SO_3H$ added by direct sulphonation. This fact affects not only the dye substantivity, but also the direction of the dipole moment vector and its size. The results of the calculations are given in Table 2 and Table 3.

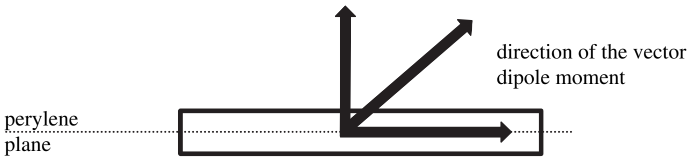
According to the analysis results (Table 4), the sulphonation reaction results in the substitution of two sulpho groups that impart water-solubility to the dye molecules. The dyes modified in this way can be used for dyeing cellulose fibres under standard conditions.

The calculation shows that the dye molecules are not fully flat, which is one of the important factors affecting their substantivity. This is particularly visible in the case of imide derivatives, in which the phenyl ring is twisted in relation to the perylene plane by about 50° [4], even for the derivatives that are not substituted with $-Cl$ and $-CH_3$. Hence the formation of dye–fibre bonds via van der Waals forces becomes difficult, which results in a low coefficient of dye combination with fibre. On the other hand, the imidazole derivatives are almost flat and their combination degree is about twice as high as that of the imide derivatives. These calculations were performed for

Table 2
Results of calculation of the geometric structure of dyes **B4–B6** and their isomers by the AM1 method



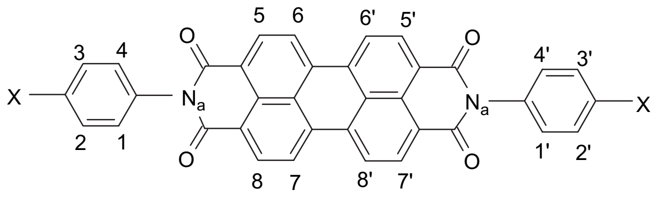
[Z - isomer] [E - isomer]

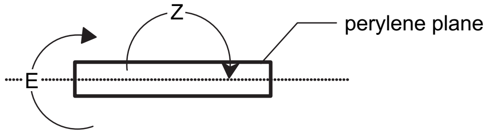


Isomer	X = SO_3H	ΔE (kJ/mol)	N_a–N_a	N–N	μ	α
Z	–	−0.54	11.34	11.65	0.14	L
E	–	**0.0**	**11.34**	**12.46**	**0.09**	**L**
E	1,1′	−10.20	11.35	12.45	2.51	∠
Z	1,1′	−10.54	11.35	11.69	9.78	=
E	1,4′	−22.38	11.35	12.47	8.55	=
Z	1,4′	−30.08	11.33	11.68	2.20	L
E	4,4′	−33.56	11.38	12.54	1.29	L
Z	4,4′	−34.27	11.40	11.70	7.61	∠
E	2,2′	−2.89	11.36	12.49	2.05	=
Z	**2,2′**	**0.0**	**11.38**	**11.73**	**5.75**	**=**
E	2,3′	−5.44	11.36	12.48	2.36	=
Z	2,3′	−6.07	11.38	11.70	1.95	∠
E	3,3′	−2.55	11.36	12.49	2.05	L
Z	3,3′	−10.25	11.35	11.68	4.20	∠
E	6,7	−97.15	11.32	12.41	1.83	L
Z	6,7	−115.69	11.24	11.60	2.67	∠
E	6,7′	−99.54	11.25	12.50	2.92	L
Z	6,7′	−98.20	11.31	11.76	2.66	∠
E	5,8′	−66.73	11.36	12.42	1.79	=
Z	5,8′	−90.21	11.39	11.74	0.76	=

α – Direction of the dipole moment vector in relation to the perylene ring plane (L – perpendicular, = – parallel, ∠ – skew).

Table 3
Results of calculation of the geometric structure of dyes **B1–B3** and their isomers by the AM1 method





Dye	X	SO_3H	ΔE (kJ/mol)	μ	$N_a–N_a$	X–X	α
B1*	H	–	–	0.14	11.38	–	L
	H	1,1′	−19.75	9.51	11.42	–	L
	H	2,1′	−10.08	3.17	11.43	–	∠
	–	X,1′	−15.40	10.14	11.40	–	∠
	H	2,2′	−7.91	2.29	11.36	–	∠
	–	X,2	−3.31	7.06	11.41	–	∠
	–	**X,X**	**0.0**	**1.41**	**11.42**	–	**L**
B2**	CH_3	–	–	0.21	11.41	22.80	∠
		1,1′[*Z*]	−12.76	8.26	11.38	22.64	L
		1,1′[*E*]	−8.62	3.57	11.40	22.75	∠
		2,1′[*Z*]	−3.60	6.93	11.40	22.75	L
		2,1′[*E*]	−4.73	1.30	11.40	22.63	=
		2,2′[*Z*]	−4.85	8.18	11.40	22.61	L
		2,2′[*E*]	**0.0**	**5.92**	**11.35**	**22.32**	∠
B3***	Cl	–	–	0.04	11.43	23.29	=
		1,1′[*Z*]	−2.84	10.39	11.39	23.17	L
		1,1′[*E*]	**0.0**	**1.17**	**11.42**	**23.23**	∠
		2,1′[*Z*]	−4.14	2.97	11.42	23.22	L
		2,1′[*E*]	−8.91	5.39	11.41	23.18	=
		2,2′[*Z*]	−10.67	7.09	11.42	23.25	∠
		2,2′[*E*]	−11.38	3.27	11.41	23.22	=

Distances X–X and $N_a–N_a$ amount to *11.21, **22.91 and 11.28 Å, ***22.96 and 11.20 Å. ΔE – Difference in energy between the molecule with the lowest energy and the molecule under examination (kJ/mol). α – Direction of the dipole moment vector in relation to the perylene ring plane (L – perpendicular, = – parallel, ∠ – skew).

the derivatives whose sulpho groups may be at the same side (*Z*) or at different sides (*E*) of the perylene core plane. This issue has not been described so far, although it seems to be of importance, especially during the initial phase of dyeing.

The results of the calculations show that not only the total molecular energy, as a measure of stability of particular isomers is changed, but also the isomer dipole moments and the directions of the dipole moment vector. Particularly, the dipole moment may be of the great importance. It may be located either in the molecule plane, or perpendicular to this plane, or at an angle from 0 to 90°. The best situation is in the case, when it is perpendicular to the molecule plane, since the projection of the dye molecule on the fibre molecule is of the largest surface and consequently there is the highest probability of mutual interactions. The most unfavourable case is when the vector sense of the dye dipole moment lies in the dye plane (resulting in the smallest surface of the dye molecule projection). This issue has not been considered in the research works so far. The interactions of this type may also affect the possible formation of specific aggregates, which take the form of piles or planes. These aggregates may in turn affect the dye exhaustion from dyebath as well as the colour effects [10–12].

From the point of view of dye application it is therefore advisable to have the dye of the high dipole

Table 4
Results of determination of sulpho groups content and spectrophotometric measurements of dyes **B1–B6** [7]

Dye	X	Quantity of $-SO_3H$ groups	λ_{max}	ε_{max}	*W*
B1	–	2.07	504	15 600	31.4
B2	CH_3	1.92	502	11 400	9.5
B3	Cl	2.00	502	12 950	16.7
B4	H	1.95	513	12 200	71.6
B5	CH_3	1.72	541	13 500	61.8
B6	Cl	2.18	540	10 900	44.7

moment and the sense of vector being perpendicular to the molecule plane.

It has been found, on the basis of the obtained results, that the condensation of the perylene anhydride and *o*-phenylenediamine gives diimidazoles **B4–B6** as isomers *E*, although the energy difference in relation to isomer *Z* is low. As it turned out the molecules of these dyes are not fully flat. This fact is confirmed by the distances between nitrogen atoms N_a–N_a in the imidazole ring. In the case of the flat molecule these distances should be 11.20 Å. The calculation results indicate also the cause of the low reactivity of perylene ring. The total molecular energies of the isomers with the sulpho groups in the polycyclic ring are considerably higher (even up to 115 kJ/mol) in relation to the derivatives with sulphonated phenyl rings. The same calculations were carried out for the imide derivatives.

The carried out calculations show that the molecule of the unsulphonated derivative **B1** itself is not fully flat and its dipole moment is $\mu > 0.0$. The sulphonation process results probably in the derivatives with sulpho groups in positions 1,1′, directed in the *trans* position to the macrocyclic ring plane. Additionally, this isomer possesses the lowest dipole moment. The least probable isomer to obtain is that one with the sulpho groups in positions 2,2′ [*E*] and with the value of $\Delta E = -11.38$ kJ/mol. Moreover, the X–X distance of **B3** is higher than that of the analogous derivatives of **B2**, despite the fact that the van der Waals radii of appropriate X groups indicate that these changes should have the opposite directions [13].

6. Conclusions

The examined dyes are characterized by the high fastnesses to washing, abrasion and light. These fastnesses are similar to those of the polycyclic dyes derived from the perylenetetracarboxylic-3,4,9,10 acid [14]. The addition of sulpho groups into the dye molecules makes them water-soluble and allows them to be used as the direct dyes. The sulphonation process results in derivatives of the number of the sulpho groups 1.72–2.18 which is adequate to make them water-soluble. The colour intensity of dyeings on the cotton fabric depends mainly on the fact whether the dye is the imide or the imidazole derivative, while the imidazole derivatives (**B4–B6**) show the higher substantivity. By means of the quantum and chemical calculations (the AM1 method) it has been shown that the imidazole derivatives possess the flat molecules contrary to the imide derivatives. In the case of the imide derivatives (**B1–B3**), the substituent at the *N*-imide atom is situated in an almost perpendicular plane to the perylene ring plane. The analysis of the molecular energy changes allows to determine the probable site of the sulpho group substitution in the dye molecules, the imide and imidazole derivatives of the perylenetetracarboxylic-3,4,9,10 acid. Attention has been also paid to the fact that the dye affinity to the cellulose fabric may depend on the sense of the vector of the molecule dipole moment.

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