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Direct Dyes Containing Cyclic Amide Groups

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ABSTRACT

Aromatic amines containing various cyclic imido systems were used as diazo components for the synthesis of several series of monoazo, disazo and trisazo dyes. Comparing the properties of the dyes with those of analogous dyes which do not contain these systems, a surprisingly high affinity of the 'imide' dyes for cellulose was observed; this was rationalised by analogy with known imidazolone pigments.

1 INTRODUCTION

Cyclic aromatic five- or six-membered imides, e.g. phthalimide, benzimidazolone, quinoxalinedione, phthalazinedione, etc., possess the ability to form stable dimers by intermolecular hydrogen bonds.[1–3] The existence of associates of this type has been confirmed by UV, IR spectra and by X-ray studies. This property has been utilised in giving high thermal fastness and low solubility of the dyes. As an example of the practical importance of such compounds, there can be mentioned the benzimidazolone pigments (Hostaperm or PV-Fast (Hoechst)).[4] As a result of forming stable dimers, these monoazo pigments have the same thermal solvent fastness as disazo pigments of the Cromophtal type (Ciba-Geigy). In previous studies[5–7] we have shown that introducing similar imide residues into disperse dyes results in a high thermal fastness, but also lowers diffusion into the substrate.

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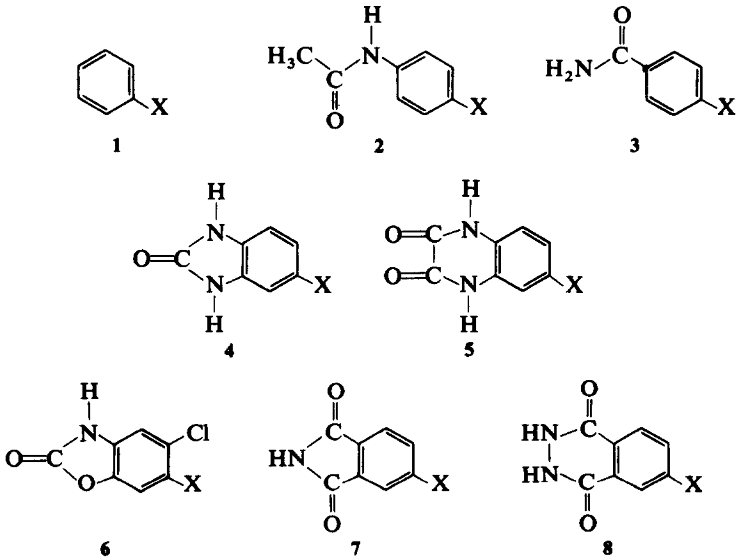
Imide residues of this type have not been used in water soluble dyes and it seemed, therefore, worthwhile to evaluate how the presence of the imide system influences the properties of such water soluble analogues.

It could be predicted that the affinity of such dyes for cellulose would improve as a result of the ability of the dye molecules to associate either between themselves or between the dye molecules and the fibre. In order to test this hypothesis, a series of mono-, dis- and trisazo dyes were synthesised, using as diazo components 5-aminobenzimidazolone (**4h**), 6-aminoquinoxalinedione (**5h**), 6-amino-5-chlorobenzoxazolone (**6h**), 4-aminophthalimide (**7h**) and 4-aminophthalazinedione (**8h**). In the synthesis of the disazo and trisazo dyes, Cleves-6 acid or *p*-cresidine were used as diazo components and J-acid and some of its derivatives as coupling components. For comparison, analogous dyes not containing imido residues were obtained using aniline (**1h**) as diazo component. In addition, dyes containing non-cyclic amide residues were synthesised and investigated, using 4-aminacetanilide (**2h**) or 4-aminobenzamide (**3h**) as diazo components. Dyes having a larger molecule and containing an additional amide system or phenylamino residue were also investigated; in order to effect this, in some cases *N*-benzoyl-J acid of *N*-phenyl-J acid were used. The influence of the structure of the dye molecule on the degree of exhaustion on cellulose fibre and on the colour and application properties were then evaluated.



Structure 1

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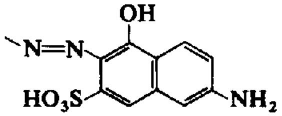
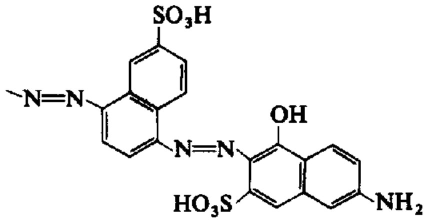
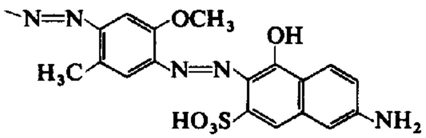
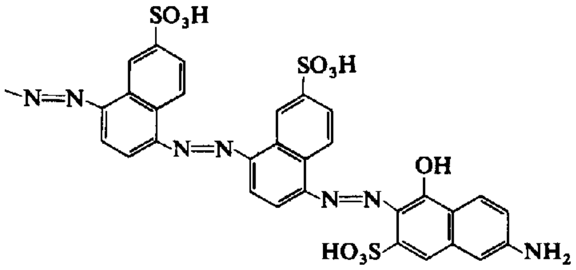
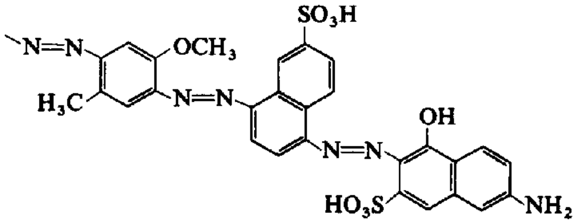
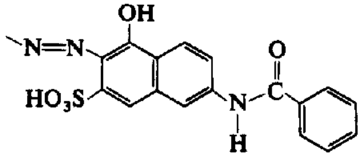
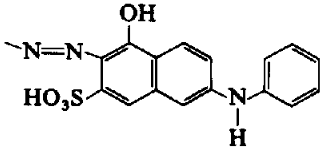
a	
b	
c	
d	
e	
f	
g	
h	—NH_2

Structure 2

2 EXPERIMENTAL

2.1 Preparing the diazo components

The aromatic amines used as diazo components were obtained and purified in the literature, viz.:

aniline (**1h**); freshly distilled; (POCh-Gliwice);

4-aminacetanilide (**2h**), technical product, crystallised from water;

4-aminobenzamide (**3h**) was obtained from 4-nitrobenzoic acid by amidation and reduction with iron;[8]

5-aminobenzimidazolone-2 (**4h**): benzimidazolone-2 was obtained by fusion of *o*-phenylenediamine with urea,[9] and then nitrated with nitric acid in sulphuric acid, followed by reduction with iron;[10]

6-aminoquinoxalinedione-1,3 (**5h**) was obtained by a similar method, in the first stage *o*-phenylenediamine being fused with oxalic acid;[11]

6-amino-5-chlorobenzoxazolone-2 (**6h**) was obtained by nitration of 5-chlorobenzoxazolone-2 and reduction of the nitro compound with iron;[12]

4-aminophthalimide (**7h**) was obtained by nitration of phthalimide and reduction of the nitro compound with stannous chloride;[13]

6-aminophthalazinedion (**8h**) was obtained by heating 4-aminophthalimide (**7h**) with boiling aqueous hydrazine;[14]

The remaining products were technically purified by crystallisation from water.

2.2 Synthesis of dyes

2.2.1 Synthesis of monoazo dyes

The more readily soluble amines (**1–3h**) (0·01 mol) were dissolved in 50 ml of water acidified with 0·03 mol (3 ml) of 30% HCl and diazotised at 0–5°C with 0·01 mol (2·5 ml) of 4 M $NaNO_2$. Less soluble amines (**4–8h**) were diazotised in a similar way, by grinding 0·01 mol of amine with 0·04 mol (4 ml) of 30% HCl and then dissolving with 50 ml of water.

The solution (or suspension) of the diazonium salt was added to a solution of 0·01 mol of 6-amino-1-naphthol-3-sulphonic acid (J acid) or its *N*-benzoyl or *N*-phenyl derivative in 100 ml of water containing 0·05 mol of NaOH. Dyes were separated from the solution by adding NaCl (*c*. 20% by volume) at 80°C. The dyes were filtered, washed with 10% NaCl and dried at 60°C.

2.2.2 Synthesis of disazo and trisazo dyes

The solution (or suspension) of the diazonium salt, prepared as above from the amines **1–8h**, was added to a solution of 0·01 mol of the sodium salt of 1-naphthylamine-6-sulphonic acid (Cleves-6 acid) or to a suspension of 0·01 mol of *p*-cresidine in 100 ml of water at 0–5°C. During coupling, pH 6–7 was maintained by portionwise addition of sodium acetate. The separated monoazo compound was filtered and the precipitate stirred with 100 ml or water and 4 ml of 30% HCl and diazotised by adding 2·5 ml of 4 M $NaNO_2$.

In the case of the synthesis of trisazo dyes, the operation of diazotisation and coupling with Cleves-6 acid was repeated.

The suspension of diazonium salt obtained from the monoazo or disazo compound was coupled with J acid in a similar way to that used for the synthesis of monoazo dyes.

2.2.3 *Analysis of dyes*

The homogeneity of the dyes was confirmed by chromatography; Whatman paper was used, with a mixture of DMF, methanol and water in 3:1:1 proportion (by volume) as eluent.[15] The content of NaCl in the dye samples was determined by potentiometry.[16]

2.2.4 *Dyeing of cotton*

Samples of bleached and mercerised cotton fabric were dyed in a Roaches-Rotec dyeing apparatus, using 1% dye (owf), a liquor ratio of 1:30 and addition of 0·5% Na_2SO_4. The dye bath was heated for 2 h to 95°C and this temperature was maintained for 1 h; it was then cooled to 20°C over 1 h. The dyed samples were rinsed thoroughly and dried. The degree of dye exhaustion from the bath (E) was determined colorimetrically on the basis of the determinations of its concentration in the bath before dyeing (c_1) and after dyeing (c_2):

$$E = \frac{c_1 - c_2}{c_2} 100\%$$

Colorimetric measurements were affected on a Specord M-40 (C. Zeiss-Jena) spectrophotometer.

2.2.5 *Determination of the fastness of dyeings*

Lightfastness of the dyeings and fastness to washing and rubbing were examined according to Polish Standards; the methods for these determinations are very similar to those used in other European countries.

3 RESULTS AND DISCUSSION

Using diazotised aromatic amines containing various cyclic imide systems (**4–8 h**) as diazo components, a series of monoazo, disazo and some

TABLE 1
Properties of Monoazo Dyes

Dye	*Exhaustion E (%)*	R_f	*Light fastness*	*Wash fastness*			*Rubbing fastness*	
				Cotton	*Change*	*Wool*	*Dry*	*Wet*
1a	48·3	0·85	3	3	3	4–5	4–5	3–4
2a	66·6	0·76	3	2–3	2	4	3	2–3
3a	79·3	0·32	4	2	2	4	3	3
4a	89·9	0·64	2–3	2	3	3	2–3	2–3
5a	90·9	0·27	—	2	2	4	2	2
6a	84·5	0·54	2	2	2	4–5	3	3
7a	45·0	0·62	2–3	4–5	4	5	4–5	4
8a	56·9	0·43	—	2	2	4–5	3	2

trisazo dyes (**4–8a–g**) were synthesised. The properties of these dyes were compared to those of analogous dyes not containing cyclic imide residues. To effect this, dyes **1a–g** using aniline as diazo component were synthesised, or dyes with a linear amide system were synthesised using 4-aminoacetanilide (**2a–g**) or 4-aminobenzamide (**3a–g**) as diazo components. For all dyes, the degree of exhaustion from the dye-bath onto

TABLE 2
Properties of Disazo Dyes

Dye	*Exhaustion E (%)*	R_f	*Light fastness*	*Wash fastness*			*Rubbing fastness*	
				Cotton	*Change*	*Wool*	*Dry*	*Wet*
1b	83·6	0·80	4–5	4	3	4–5	3	3
2b	91·8	0·69	4–5	2	3	5	2–3	3
3b	83·0	0·73	3–4	3	3	5	3	3
4b	99·0	0·65	4–5	3	3	5	3–4	3–4
5b	75·2	0·24	4	2–3	3	5	3–4	3
6b	68·3	0·38	4	2–3	3	5	3	3
7b	67·2	0·74	3–4	3–4	3	5	3	3–4
8b	93·3	0·45	—	2	2	5	4–5	4
1c	97·4	0·31	3–4	2	3	2	2–3	2
2c	98·7	0·22	3	2	4	4	3	2
3c	75·3	0·17	—	3	4	2	3	2–3
4c	99·5	0·16	3	2	4	4–5	2–3	2
5c	87·0	0·16	2	2	3	5	2	2
6c	78·2	0·24	2	2	3	5	2–3	3
7c	89·0	0·10	3	3	3	5	2–3	2
8c	98·9	0·16	—	2	2	5	4	3

cellulose was determined, and their R_f constants and their lightfastness and fastness to washing and rubbing were also determined.

The greatest differences between the different types of dyes were observed when comparing their dyeing properties. Comparing the degree of exhaustion, a considerable increase in the degree of exhaustion was noted in the case of dyes containing the imidazolone (**4**), quinoxalinedione (**5**) and benzoxazolone systems (**6**). This was particularly apparent for the data concerning the exhaustion of the simpler monoazo dyes (**1–8a**), as shown in Table 1.

The dyes containing imidazolone, quinoxalinedione or benzoxazolone systems (**4–6a**) exhausted to *c.* 90%, whilst the analogous dye no containing imido residues (**1a**) exhausted *c.* 50%, and dyes with the 'linear' amido system (**2a** and **3a**) exhausted in the 65–80% region. It should be noted that the increased exhaustion from the dyebath is observed where there are present two readily available NH groups (or NH and O) in the imido system adjacent to the aromatic ring (dyes **4–6a**). However, the presence of (i) one NH group (**7a**) or (ii) of two adjacent NH groups, separated from the aromatic ring by carbonyl groups (**8a**) or (iii) the presence of the linear amido groups (**2a** and **3a**) does not result in an increase in exhaustion compared to the dye without amido groups (**1a**).

TABLE 3
Properties of Trisazo Dyes

Dye	*Exhaustion E (%)*	R_f	*Light fastness*	*Wash fastness*			*Rubbing fastness*	
				Cotton	*Change*	*Wool*	*Dry*	*Wet*
1d	94·4	0·64	5	2–3	3	5	2	2–3
2d	90·3	0·54	5	3	4	5	2	3
3d	96·1	0·25	5	3	3	5	2	2–3
4d	97·5	0·58	4–5	3–4	4	5	2–3	3
5d								
6d								
7d	78·2	0·44	4–5	3–4	3	5	2–3	3
8d								
1e	91·6	0·23	4–5	3	2	5	3	2–3
2e	88·3	0·19	4–5	3	2	5	2–3	2
3e	93·8	0·23	4–5	2	4	4	2	2–3
4e	98·0	0·14	4–5	3–4	4–5	5	4	2
5e								
6e								
7e	80·3	0·16	4–5	3	3	5	3	2–3
8e								

TABLE 4
Properties of Monoazo Dyes from *N*-benzoyl J Acid and *N*-phenyl J Acid

Dye	*Exhaustion E (%)*	R_f	*Light fastness*	*Wash fastness*			*Rubbing fastness*	
				Cotton	*Change*	*Wool*	*Dry*	*Wet*
1f	83·7	0·78	3–4	2	3	2–3	3–4	3
2f	90·4	0·69	4	2	4	2–3	3	2–3
3f	91·0	0·52	3	2	4	3	2–3	2
4f	99·3	0·41	4	2	2	2	3–4	3
5f								
6f								
7f	33·6	0·65	4	3–4	3	4–5	4–5	4–5
8f								
1g	77·9	0·82	3–4	2	3	3	3	2–3
2g	91·9	0·80	3–4	1–2	3	2	3	2–3
3g	92·1	0·67	3	2	3	2	3	2–3
4g	96·0	0·60	4	2	2	3–4	3	2
5g								
6g								
7g	39·3	0·85	3–4	4	4	4–5	4–5	4–5
8g								

This confirms the importance of the cyclic —HN—CO—NH— system with respect of the dye affinity for the fibre. The lower influence of the related —CO—NH—CO— and —CO—NH— systems may be a consequence of the fact that in the process of bonding of the dye with the fibre, two different bonds via NH or O groups play a significant role; they probably form the dimers of the dye, as well as dye–fibre bonds.

A similar increase in affinity of the imido dyes was observed for some of the disazo dyes (**1–8b** and **1–8c**) (Table 2). However in this case, the exhaustion was quite good for all dyes because of the increase in their molecular weight, so differences between the exhaustion of the 'imide' (**4–6**) and 'phenyl' (**1**) dyes are not as large as in the case of monoazo dyes. It is apparent however that the dyes containing the benzimidazolone moiety (**4b** and **4c**) have the best exhaustion.

To confirm these results, selected trisazo dyes were synthesised, using aniline (**1h**), 4-aminoacetanilide (**2h**), 4-aminobenzamide (**3h**), 4-aminobenzimidazolone (**4h**) and 4-aminophthalimide (**7h**) as diazo components (dyes **1–4** and **7d** and **1–4** and **7e** in Table 3). In all cases the best results were obtained for the imidazolone dyes (**4**) are observed, as in the monoazo and disazo dyes, although there were small differences in exhaustion between individual dyes.

Evaluation of the degree of exhaustion of the monoazo dyes obtained with the use of benzoyl-J acid (**1–4** and **7e**) and *N*-phenyl-J–acid (**1–4** and **7g**) gave the same conclusions (Table 4), i.e. all dyes based on the J-acid derivatives (**1–4f** and **1–4g**) have a slightly better degree of exhaustion compared to the dyes based on unsubstituted J acid (**1–4a**), but the exhaustion of the 'imidazolone' dyes (**4**) is always superior. The 'phthalimide' dyes (**7f** and **7g**) showed a surprisingly low degree of exhaustion.

A quite good correlation can be observed between the degree of dye exhaustion and the R_f value of the dye. Generally, a high R_f value is accompanied by a low degree of exhaustion. In practice, however, some significant exceptions from this can be observed. It is well known that the relationship between R_f value alone and dye affinity is not simple enough to draw explicit conclusions about the dye affinity to cellulose.[15]

The lightfastness of the dyeings were similar within each type of dye. In most cases, there was no significant difference between the fastness of the dyeings from dyes containing an imido system and those lacking that system. The fastness was higher for the dyes with a more extended

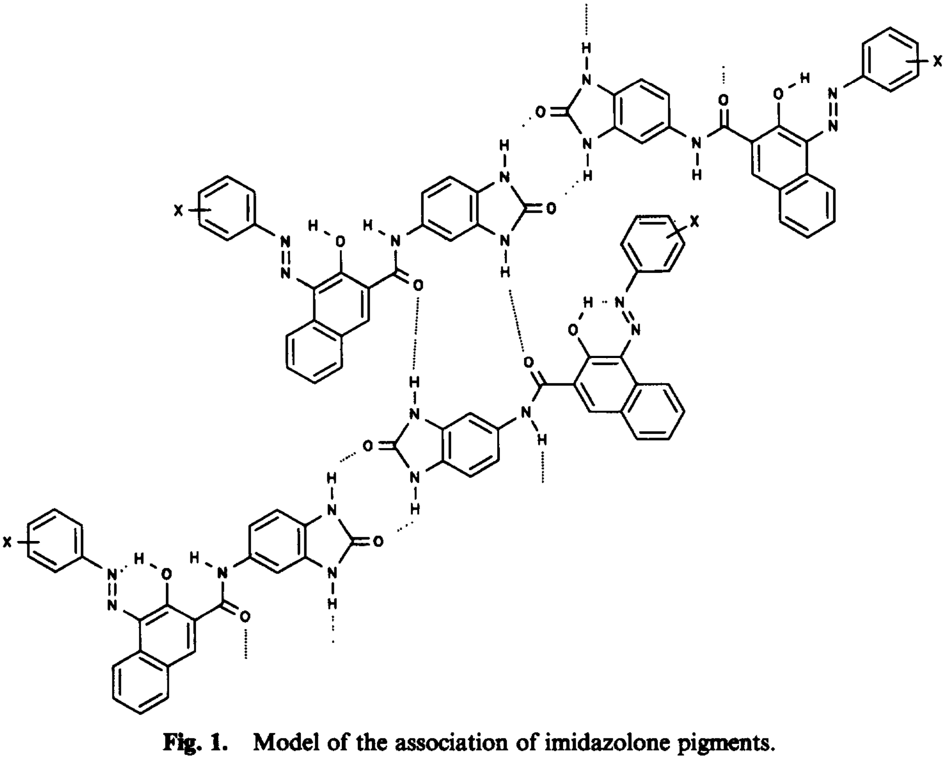


Fig. 1. Model of the association of imidazolone pigments.

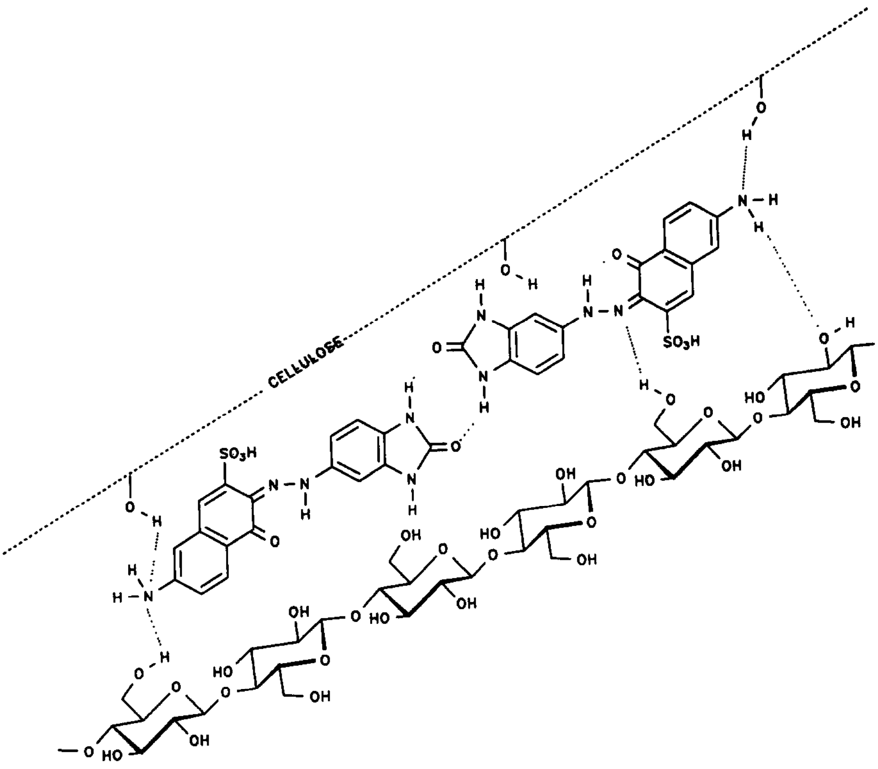


Fig. 2. Model of the association of imidazolone dyes.

system, i.e. the polyazo dyes **d** and **e**, and also in the case of dyes in which the amino group was acylated or arylated (**f** and **g**).

Fastness of the dyeings to washing and rubbing were similar for analogous 'imide' and 'phenyl' dyes, differences not exceeding 0·5–1 units; the values do not allow any general conclusions to be drawn as to the influence of the presence of the imido system on this fastness.

4 CONCLUSIONS

The results of the investigations indicate that dyes containing a cyclic imide system, e.g. imidazolone, quinoxalinedione or benzoxazolone show significant dye affinity to cellulose, even in cases where the dye has a relatively small molecular size. In some cases, monoazo dyes containing the imido-system (**4a**, **5a**, **4f**, **fg**) exhausted onto cellulose as well as typical trisazo direct dyes. For example, the monoazo 'imidazolone' dye **4a** shows an exhaustion of *c*. 90%, close to that of the 'phenyl' disazo dye

1d (*c*. 94·5%) whilst the degree of exhaustion of the analogous monoazo dye **1a** lacking the imido system is below 50%.

By analogy with established imidazolone pigments (Hostaperm), it can be concluded that the high affinity to cellulose of the dyes with a cyclic imide system results from the ability of their molecules to associate. Moreover, as with other investigated pigments[3] (Fig. 1), they can probably form dimers and these dimers can be durably bound with cellulose molecules through hydrogen bonds. A highly probable mode of binding with cellulose comprises the formation of a dimer by one of the NH groups, while the second NH group forms the bond between the dimer and cellulose (Fig. 2). Such a proposition makes it possible to explain the particularly good affinity to cellulose shown by dyes containing the imidazolone system (**4**), which ensures an uninterrupted interaction of the two NH groups, forming various types of associates.

The results of the investigation indicate the possibility of obtaining practically useful dyes,[17] especially because the fastness of the dyeings from the 'imide' dyes is in all cases close to those of the dyeings of analogous 'phenyl' dyes.

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