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Structure Optimization in a Series of Dyes for Wool and Cotton. A Chemometric Approach

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ABSTRACT

Fastness properties on wool and cotton of a series of acid dyes, previously designed by a chemometric approach and tested on silk, have been studied.

Wash fastness and light fastness data of the training set have been modelled as a function of the structure by the partial least squares (PLS) method. The models established have been used successfully to predict the fastness of new dyes of the series.

Comparisons within the fastness performance of the series on the three fibres have allowed the identification of the best dyes for each of the fibres.

INTRODUCTION

In a recent paper[1] a series of acid dyes for silk was studied using a chemometric approach. The strategy consisted of selecting a small number of dyes by the technique of Experimental Design, using the Principal Properties of the substituents as design variables. The selected dyes were synthesized and their fastness properties on silk measured. Wash fastness and light fastness values were related to the chemical structure by the partial least squares (PLS) method.

The QSAR developed allowed the prediction of the structure of dyes with high fastness performance. The synthesis of the predicted dyes confirmed the validity of the predictions. The selection of molecules that provide the most useful information is the crucial step, because the prediction capability of QSAR models depends heavily on the molecules selected for model building.

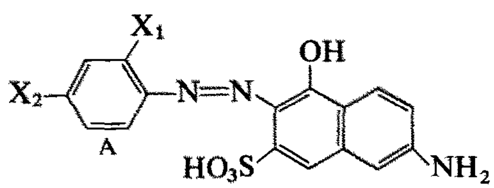
Application of the techniques of Experimental Design and the use of the Principal Properties as structure descriptors are powerful tools to reduce the number of molecules to be synthesized and tested, leading to a considerable resource saving. In the case reported, eight dyes were selected as representatives of a large class of dyes. The models established for this training set gave information about the whole series. The final result was the identification of two dyes, one in the training set, the other in the predicted set, as the optimum dyes of the series.

In the present paper, the study of the fastness performance of the above class of dyes was extended to wool and cotton. The same training set of eight dyes has been used to build QSAR models for each of the fibres. The established models allowed predictions of new dyes which were synthesized and tested.

PROCEDURES

Training set

The selection of dyes of the training set, of general formula **I**, has been described previously.[1]



(I)

The matrix of the Fractional Factorial Design in coded form, and the selected substituents, are shown in Table 1. The design variables, PP1 and PP2, are linear combinations of the traditional structure descriptors (σ_m, σ_p, π, MR, Verloop parameters) obtained by principal component analysis.[2]

PLS analysis

PLS analysis was used to model the fastness data of the training set as a function of the structure. PLS is a regression method, based on PCA,

TABLE 1
Matrix of the Fractional Factorial Design and Corresponding Selected Substituents

Dye	X_1		X_2		*Substituents*	
	PP1	*PP2*	*PP1*	*PP2*	X_1	X_2
1	−	−	−	−	NO_2	NO_2
2	+	−	−	+	COC_6H_5	H
3	−	+	−	+	H	H
4	+	+	−	−	C_6H_5	NO_2
5	−	−	+	+	NO_2	C_6H_5
6	+	−	+	−	$OCOC_6H_5$	$OCOC_6H_5$
7	−	+	+	−	H	COC_6H_5
8	+	+	+	+	OC_3H_7	OC_3H_7

aimed at detecting cause-and-effect relationships between a *y* variable or a Y block (fastness data) and an X block (structure descriptors). The PLS method has already been described.[1,3]

Structure description

For the structure description, the physicochemical parameters of the substituents,[4] listed in Table 2, were used, as well as a series of calculated molecular parameters listed in Table 3.

TABLE 2
Substituent Descriptor Values

Substituent	σ_m	σ_p	π	*MR*	*L*	*B1*	*B2*	*B3*	*B4*
NO_2	0·71	0·78	−0·28	7·36	3·44	1·70	1·70	2·44	2·44
COC_6H_5	0·34	0·43	1·05	30·33	4·57	2·36	3·11	3·11	5·98
H	0	0	0	1·03	2·06	1·00	1·00	1·00	1·00
C_6H_5	0·06	−0·01	1·96	25·36	6·28	1·70	1·70	3·11	3·11
$OCOC_6H_5$	0·21	0·13	1·46	32·33	8·15	1·70	1·70	1·84	4·40
OC_3H_7	0·10	−0·25	1·05	17·06	6·05	1·35	1·90	1·90	4·30
Cl[a]	0·37	0·23	0·71	6·03	3·52	1·80	1·80	1·80	1·80
CN[a]	0·56	0·66	−0·57	6·33	4·23	1·60	1·60	1·60	1·60

[a] Substituents present in the designed dyes.

TABLE 3
Calculated Molecular Parameters of Dyes

Dye	ΔH_f[a]	I.P.[b]	Dipole[c]	Area[d]	Volume[e]
1	−30·93	8·9	9·7	379·7	309·8
2	−44·67	8·5	4·0	429·5	360·5
3	−43·36	8·5	5·6	327·2	272·0
4	−11·35	8·8	11·7	438·0	361·3
5	−13·07	8·7	2·9	435·5	361·3
6	−125·21	8·4	6·9	555·7	464·6
7	−44·65	8·7	6·5	431·4	359·8
8	−142·29	8·3	4·4	478·9	387·4
9*	−17·75	8·5	5·5	411·1	343·5
10*	−44·01	8·9	11·0	372·8	305·6
11*	−38·23	8·8	5·8	456·3	380·0
12*	−4·79	8·9	10·3	378·2	307·9
13*	−56·17	8·6	6·1	362·3	301·9

[a] Heat of formation in kcal/mol.
[b] Ionization potential in eV.
[c] Dipole in Debye.
[d] van der Waals area in Ångstrom^2.
[e] Volume in Ångstrom^3.
* Designed dyes.

EXPERIMENTAL

Dye synthesis

Preparation of dyes **1–11** has been previously reported.[1-5] Dye **12** was prepared by diazotization of 2-cyano-4-nitroaniline with nitrosylsulphuric acid. Sodium nitrite (0·87 g) was added portionwise with stirring to concentrated sulphuric acid (5 ml) and the temperature of the reaction mixture was allowed to rise to 65°C. 2-Cyano-4-nitroaniline (1·64 g, 0·01 mol) in concentrated sulphuric acid (5 ml) was added with stirring to the solution cooled to 0°C. After stirring at 0–5°C for 60 min a clear solution was obtained. The diazonium solution was then added, with stirring at 10°C, to a solution of 7-amino-4-hydroxy-2-naphthalene-sulphonic acid (2·4 g, 0·01 mol) in aqueous NaOH (0·4 g in 50 ml of water), at pH 8. Dye **13** was synthesized by diazotization of 2,4-dichloro-aniline[6] and subsequent coupling with 7-amino-4-hydroxy-2-naphthalene-sulphonic acid, at pH 8.

The crude dyes were purified by the method reported previously.[5] Purity was checked by thin layer chromatography. The visible absorption maxima and absorptivities, reported in Table 4, were recorded on a Hitachi U-3200 spectrophotometer from aqueous solutions.

TABLE 4
Spectroscopic Data of Dyes

Dye	λ_{max} (nm)	log ε
1	523·5	3·93
2	488·4	4·00
3	481·5	4·17
4	474·2	3·54
5	506·8	3·79
6	540·6	4·30
7	485·4	4·03
8	529·5	4·18
9*	489·6	4·19
10*	521·6	4·04
11*	530·4	4·01
12*	524·4	4·02
13*	482·4	3·78

* Designed dyes.

Dyeing of wool

The wool samples were dyed in a refluxing thermostatted bath with a 100:1 liquor ratio (3% dye, 10% Na_2SO_4 concentration), pH 3–3·5. The samples were placed into the dyebath at 60°C; the temperature was allowed to rise to 95°C and maintained for 60 min. The patterns were then removed, rinsed in cold water and dried.

Dyeing of cotton

The cotton samples were dyed in a thermostatted bath at 95°C for 60 min, with a 100:1 liquor ratio (5% dye, 20% NaCl concentration).

Fastness assessment

Fastness to light, to washing and to perspiration were measured according to standard procedures.[7] The fastness data on wool and cotton are listed in Tables 5 and 6, respectively.

Calculations

PLS analysis was carried out on a COMPAQ 4/66 computer using the SIMCA-3B package developed by Wold and co-workers at the University

TABLE 5
Change in Shade on Wool of the Training Set Dyes

Dye	*Wash*			*Dry cleaning*	*Perspiration*		*Light*
	Mild	*Medium*	*Strong*		*Acid*	*Alkaline*	
1	5	4–5	3–4	5	5	5	6–7
2	5	4–5	4	5	5	5	3–4
3	5	4	3	4–5	5	4	4
4	4–5	4	2	4	4–5	4–5	3
5	4–5	4	3	4–5	4–5	4–5	5
6	5	5	4	5	5	5	7–8
7	4–5	4	3–4	4–5	5	4–5	4–5
8	4	3	2	4	4–5	4–5	4–5

of Umeå. Molecular parameters were calculated by means of semiempirical MO methods. The AM1 Hamiltonian, as implemented in the MOPAC V6.0 package,[8] was used. All the geometries were optimized without constraints. In Table 3 the resulting heats of formation, ionization potentials and dipoles are reported, together with the van der Waals surface areas and volumes of the optimized geometries. The van der Waals radii were taken from the literature.[9] The volume was calculated with a grid of 0·1 Å. The calculations were performed on a MicroVAX 3100-40 running VMS operating system. The semiempirical MO calculations were carried out using the MOPAC V6.0 program, while a MacroModel V3.1 interactive molecular modelling package[10] was used to calculate areas and volumes.

TABLE 6
Change in Shade on Cotton of the Training Set Dyes

Dye	*Wash*			*Dry cleaning*	*Perspiration*		*Light*
	Mild	*Medium*	*Strong*		*Acid*	*Alkaline*	
1	5	4–5	4	5	5	5	3–4
2	3[a]	2–3[a]	1–2[a]	4–5	4–5	4[a]	2
3	4[a]	3–4[a]	3[a]	5	4–5	4–5	2–3
4	3–4	2–3	1–2	4	5	4–5	1–2
5	4–5	4	3–4	5	5	5	3
6	5	5	4	5	5	5	5
7	4	3	2	5	5	5	2–3
8	4	3	2	4–5	4–5	4–5	3–4

[a] Unlevel dyeing.

RESULTS AND DISCUSSION

PLS modelling of fastness on wool

Fastness to washing

Medium and strong washing fastness data of the training set (Y block, Table 5) were modelled as a function of the structure descriptor variables (X block, Tables 2 and 3). Mild washing, as well as dry cleaning and

TABLE 7

Wash Fastness on Wool: Variable Loadings p^a and Corresponding Modelling Powers ψ^b for each Component of the PLS Model

	p_1	ψ_1	p_2	ψ_2	p_3	ψ_3	p_4	ψ_4
y variables								
Medium	0·85	0·13	0·54	0·15	0·64	0·40	0·97	0·80
Strong	0·53	0·00	0·84	0·13	0·77	0·57	0·23	0·53
x variables								
X_1 σ_m	0·30	0·19	0·28	0·38	−0·21	0·42	−0·14	0·46
σ_p	0·30	0·19	0·32	0·49	−0·11	0·47	−0·08	0·43
π	0·13	0·00	−0·40	0·35	0·06	0·29	0·14	0·28
MR	0·30	0·19	−0·27	0·37	0·18	0·38	0·04	0·29
L	0·20	0·03	−0·25	0·12	0·04	0·02	0·09	0·00
B1	0·43	0·65	−0·09	0·68	0·04	0·65	−0·09	0·70
B2	0·34	0·29	−0·18	0·33	0·08	0·27	−0·21	0·41
B3	0·38	0·43	−0·19	0·55	−0·24	0·74	−0·03	0·72
B4	0·30	0·20	−0·24	0·31	0·14	0·28	−0·16	0·30
X_2 σ_m	0·09	0·00	−0·05	0·00	−0·33	0·00	0·42	0·48
σ_p	0·10	0·00	−0·02	0·00	−0·23	0·00	0·44	0·40
π	−0·05	0·00	0·26	0·00	−0·12	0·00	−0·17	0·00
MR	−0·06	0·00	0·26	0·00	−0·12	0·00	0·10	0·00
L	0·02	0·00	0·14	0·00	−0·11	0·00	0·01	0·00
B1	−0·07	0·00	0·25	0·00	−0·34	0·04	0·32	0·40
B2	−0·19	0·02	0·18	0·01	−0·32	0·05	0·23	0·13
B3	−0·03	0·00	0·26	0·00	−0·56	0·48	0·17	0·65
B4	−0·16	0·00	0·16	0·00	−0·22	0·00	0·17	0·00
ΔH_f	0·11	0·13	0·15	0·00	−0·19	0·00	0·12	0·00
Dipole	0·08	0·00	−0·14	0·00	−0·07	0·00	0·47	0·56
vdW Area	0·13	0·00	−0·05	0·00	−0·00	0·00	0·06	0·00
vdW Volume	0·14	0·00	−0·03	0·00	0·04	0·00	0·07	0·00
Variance explained %	12·2		26·7		73·0		87·1	

[a] Variable loadings p express the extent and sign of correlation between y and x variables.
[b] Modelling powers ψ indicate the relevance of the variables in the PLS model. $\psi_{ia} = (1 - s_i/s_i^{\circ})$, where s_i and s_i° are respectively the standard deviation after extracting a component and standard deviation of data, for variable i.

perspiration data, were not modelled as they showed a low variability along the set, with scores near the top of the scale.

A four component model was calculated explaining about 87% of the total Y variance. Variable loadings and modelling powers are reported in Table 7. The most important variables (highest modelling power values) appear to be X_1-substituent descriptors and X_2-steric parameters; the molecular dipole also contributes to the model.

Fastness to light

Light fastness data (y) were modelled as a function of the structure descriptors (X block) by a three component model, explaining about 93% of the y variance. The results of the PLS analysis are reported in Table 8. The most important variables appear to be the electronic

TABLE 8

Light Fastness on Wool: Variable Loadings p and Corresponding Modelling Powers ψ for each Component of the PLS Model

	p_1	ψ_1	p_2	ψ_2	p_3	ψ_3
y variable	1	0·20	1	0·44	1	0·74
x variables						
X_1 σ_m	0·09	0·00	0·52	0·51	−0·27	0·80
σ_p	0·04	0·00	0·52	0·42	−0·32	0·73
π	−0·02	0·00	−0·27	0·00	−0·01	0·00
MR	0·02	0·00	−0·03	0·00	−0·09	0·00
L	0·14	0·00	−0·06	0·00	0·09	0·00
B1	−0·05	0·00	0·26	0·00	−0·38	0·00
B2	0·10	0·00	0·14	0·00	−0·33	0·00
B3	−0·08	0·00	0·19	0·00	−0·45	0·11
B4	−0·01	0·00	0·05	0·00	−0·15	0·00
X_2 σ_m	0·04	0·00	0·06	0·00	−0·04	0·00
σ_p	−0·01	0·00	0·07	0·00	−0·09	0·00
π	0·33	0·36	−0·05	0·30	−0·08	0·23
MR	0·39	0·66	−0·13	0·74	0·00	0·71
L	0·38	0·57	−0·02	0·53	0·10	0·51
B1	0·29	0·25	−0·14	0·22	−0·13	0·17
B2	0·27	0·18	−0·28	0·29	−0·07	0·21
B3	0·28	0·20	−0·03	0·12	−0·30	0·20
B4	0·35	0·41	−0·27	0·64	0·05	0·60
ΔH_f	−0·14	0·00	0·16	0·00	−0·40	0·07
Dipole	0·00	0·00	−0·01	0·00	0·15	0·00
vdW Area	0·29	0·24	−0·14	0·22	−0·01	0·13
vdW Volume	0·29	0·23	−0·13	0·20	0·02	0·11
Variance explained %	36·0		68·2		93·1	

TABLE 9
Calculated Values of Fastnesses on Wool for the Training Set and Residuals

Dye	*Fastness to washing*				*Fastness to light*	
	Medium		*Strong*			
	calc.	*Δ*[a]	*calc.*	*Δ*[a]	*calc.*	*Δ*[a]
1	4·6	−0·1	3·5	0·0	6·3	0·2
2	4·5	0·0	3·7	0·3	3·1	0·4
3	3·9	0·1	3·3	−0·3	4·2	−0·2
4	3·9	0·1	2·1	−0·1	3·1	−0·1
5	3·9	0·1	3·2	−0·2	5·4	−0·4
6	5·0	0·0	4·2	−0·2	6·8	0·2
7	4·0	0·0	3·1	0·4	4·2	0·3
8	3·1	−0·1	1·9	0·1	4·7	0·2

[a] Δ = difference between experimental and calculated value.

parameters of the X_1-substituent and the steric parameters of X_2-substituent.

Validation and predictions

The two QSAR models were used to recalculate the fastness values of the training set and to predict the values of new compounds of the series. The calculated values are listed in Table 9. The residuals (experimental minus calculated values) show that the models can be used for predictive purposes. Among the predicted dyes, five were synthesized and the corresponding fastnesses measured. The predicted and experimental data, listed in Table 10, show that the predictions are quite satisfactory.

TABLE 10
Structures and Fastness Predicted and Experimental Values of the Designed Dyes for Wool

Dye	X_1	X_2	*Fastness to washing*				*Fastness to light*	
			Medium		*Strong*			
			calc.	*exp.*	*calc.*	*exp.*	*calc.*	*exp.*
9	H	C_6H_5	3·4	3–4	2·5	2–3	4·2	4
10	Cl	NO_2	4·3	4–5	3·3	3–4	5·1	5
11	NO_2	COC_6H_5	4·5	4–5	3·6	3–4	5·6	6
12	CN	NO_2	4·8	4–5	4·2	3–4	6·9	7
13	Cl	Cl	4·1	4	3·2	3	4·8	4–5

TABLE 11
Wash Fastness on Cotton: Variable Loadings p and Modelling Powers ψ for each Component of the PLS Model

	p_1	ψ_1	p_2	ψ_2	p_3	ψ_3
y variables						
Mild	0·67	0·30	0·44	0·45	0·60	0·78
Medium	0·54	0·15	0·60	0·42	0·60	0·71
Strong	0·51	0·12	0·67	0·49	0·54	0·78
x variables						
X_1 σ_m	0·13	0·00	0·47	0·43	−0·31	0·71
σ_p	0·09	0·00	0·45	0·33	−0·34	0·61
π	−0·18	0·02	−0·16	0·00	0·13	0·00
MR	−0·16	0·00	0·06	0·00	0·06	0·00
L	−0·02	0·00	0·03	0·00	0·21	0·00
B1	−0·16	0·02	0·30	0·10	−0·34	0·21
B2	−0·23	0·09	0·19	0·08	−0·35	0·20
B3	−0·17	0·01	0·22	0·02	−0·36	0·12
B4	−0·18	0·03	0·13	0·00	−0·14	0·00
X_2 σ_m	0·06	0·00	−0·03	0·00	0·04	0·00
σ_p	0·04	0·00	−0·02	0·00	−0·02	0·00
π	0·31	0·26	−0·02	0·19	−0·10	0·11
MR	0·37	0·46	−0·14	0·49	0·00	0·43
L	0·31	0·26	0·01	0·20	0·13	0·13
B1	0·33	0·33	−0·23	0·44	−0·13	0·42
B2	0·29	0·22	−0·37	0·61	−0·12	0·62
B3	0·33	0·34	−0·11	0·31	−0·28	0·43
B4	0·32	0·30	−0·31	0·60	0·02	0·55
ΔH_f	−0·03	0·00	0·11	0·00	−0·35	0·00
Dipole	−0·01	0·00	−0·05	0·00	0·27	0·00
vdW Area	0·14	0·00	−0·07	0·00	0·04	0·00
vdW Volume	0·14	0·00	−0·07	0·00	0·04	0·00
Variance explained %	34·1		70·0		94·0	

Conclusions

Information obtained by the described procedure can be summarized as follows:

The series shows a high general performance as far as washing fastness is concerned, taking into account that strong washing conditions are not practicable for wool.

The series shows a greater variability in light fastness values: the maximum score (7–8) is shown by dye **6**, the minimum (3) by dye **4**.

The predictions allowed the identification of dye **12** with high wet and light fastness. The best dye of the series appears to be **6**.

TABLE 12
Light Fastness on Cotton: Variable Loadings p and Modelling Powers ψ for each Component of the PLS Model

	p_1	ψ_1	p_2	ψ_2	p_3	ψ_3
y variable	1	0·27	1	0·56	1	0·80
x variables						
X_1 σ_m	−0·02	0·00	0·42	0·06	−0·06	0·00
σ_p	−0·09	0·00	0·37	0·04	−0·08	0·00
π	0·09	0·00	−0·38	0·06	0·14	0·00
MR	0·13	0·00	−0·16	0·00	0·05	0·00
L	0·23	0·12	−0·11	0·05	0·20	0·03
B1	−0·02	0·00	0·04	0·00	−0·12	0·00
B2	−0·02	0·00	0·00	0·00	−0·23	0·00
B3	−0·08	0·00	−0·11	0·00	−0·04	0·00
B4	0·11	0·00	−0·03	0·00	−0·12	0·00
X_2 σ_m	−0·09	0·00	−0·22	0·00	0·48	0·33
σ_p	−0·15	0·00	−0·23	0·00	0·42	0·30
π	0·33	0·40	0·11	0·37	−0·24	0·51
MR	0·35	0·48	−0·06	0·43	0·01	0·37
L	0·38	0·69	0·09	0·69	0·06	0·68
B1	0·16	0·01	−0·27	0·02	0·19	0·00
B2	0·17	0·03	−0·33	0·09	0·09	0·00
B3	0·12	0·00	−0·17	0·00	0·06	0·00
B4	0·30	0·30	−0·23	0·33	0·09	0·28
ΔH_f	−0·27	0·19	−0·08	0·13	−0·05	0·03
Dipole	−0·07	0·00	−0·23	0·00	0·56	0·68
vdW Area	0·36	0·52	−0·15	0·54	0·05	0·50
vdW Volume	0·35	0·49	−0·14	0·50	0·04	0·45
Variance explained %	46·1		81·0		96·0	

PLS modelling of fastness on cotton

Fastness to washing

The three wash fastnesses (Y block) were modelled as a function of the structure descriptors (X block) by a three component model, explaining about 94% of the total y variance. The results of the PLS analysis are reported in Table 11. The most important variables appear to be the steric parameters of the X_2-substituent and the electronic ones of the X_1-substituent.

Fastness to light

Lightfastness data (y) were modelled as a function of the structure descriptors (X block) by a three component model, explaining about 96% of the y variance. The results of the PLS analysis are listed in Table 12.

TABLE 13
Calculated Values of Fastnesses on Cotton for the Training Set and Residuals

	Fastness to washing						*Fastness to light*	
	Mild		*Medium*		*Strong*			
Dye	*calc.*	Δ^a	*calc.*	Δ^a	*calc.*	Δ^a	*calc.*	Δ^a
1	4·8	0·2	4·5	0·0	3·9	0·1	3·5	0·0
2	3·0	0·0	2·3	0·2	1·4	0·1	1·8	0·2
3	4·1	−0·1	3·6	−0·1	2·8	0·2	2·5	0·0
4	3·5	0·0	2·6	−0·1	2·8	0·2	1·7	−0·2
5	4·7	−0·2	4·2	−0·2	3·6	−0·1	3·3	−0·3
6	5·0	0·0	4·7	0·3	4·0	0·0	4·9	0·1
7	3·9	0·1	2·9	0·1	1·8	0·2	2·4	0·1
8	4·0	0·0	3·2	−0·2	2·3	−0·3	3·5	0·0

[a] Cf Table 9.

The most important feature appears to be substitution at the X_2 position; molecular parameters such as surface, volume and dipole also contribute to the model.

Validation and predictions
The values of fastnesses of the training set calculated by the PLS models are listed in Table 13. The residuals show a good agreement between calculated and experimental values.

Predictions of fastness values were made for new dyes and the properties of dyes **9–12** were measured. Predicted and experimental values, listed in Table 14, show a good agreement.

TABLE 14
Fastness Predicted and Experimental Values of the Designed Dyes for Cotton

Dye[a]	*Fastness to washing*						*Fastness to light*	
	Mild		*Medium*		*Strong*			
	calc.	*exp.*	*calc.*	*exp.*	*calc.*	*exp.*	*calc.*	*exp.*
9	4·5	4–5	3·8	4	3·0	3	2·6	2–3
10	4·2	4	3·5	3–4	2·7	3	2·5	2–3
11	4·3	4	3·4	3	2·6	2–3	3·0	3
12	5·0	5	4·7	4–5	4·1	4	3·9	4

[a] For structures see Table 10.

Conclusions
Information obtained can be summarized as follows:

The series shows a generally moderate wet fastness, except for dyes **6**, **1**, and **12**.

Lightfastness values are generally low, the highest scores being 5 and 4 for dyes **6** and **12** respectively.

Dyes **6** and **12** appear, therefore, to be the optimum dyes of the series on cotton.

GENERAL CONCLUSIONS

The results obtained on cotton and on wool, compared with those on silk, previously reported,[1] lead to some considerations. The series of dyes examined shows different behaviour on the three fibres tested, as was foreseen. The different physical and chemical nature of the fibres requires the development of structurally and chemically distinct dyes for colouring specific fibres.

Direct dyes for cellulose fibres are anionic dyes with higher molecular masses and more linear structures than dyes used for wool. The highest affinity is shown by structures bearing groups that are most likely to form hydrogen bonds with the hydroxyl groups of cellulose, spaced at intervals corresponding approximately to the hydroxyl group spacing in cellulose.[11]

Acid dyes for protein fibres are anionic molecules, with molecular masses generally in the range 350–900,[12] and which are substantive to the protein by means of a combination of polar and hydrophobic interactions.[13]

The series of dyes examined showed the best general performance on wool, while it appeared less suitable for application to cotton. In fact these dyes have a generally low molecular mass and structures which are not particularly suitable to form hydrogen bonds with the hydroxyl groups of cellulose.

The exceptionally good properties of dye **6** with regard to substantivity, brightness, wet and light fastness on cotton, can be attributed both to a higher molecular mass and to a more extended linear structure, as can be seen in Fig. 1.

The performance of the dyes on the two protein fibres is different as far as wet and light fastnesses are concerned. Dye **6**, which is the best dye of the series on wool, is the worst on silk; on the other hand dyes **7** and **11**, which give the best results on silk, show only moderate values of fastness on wool.

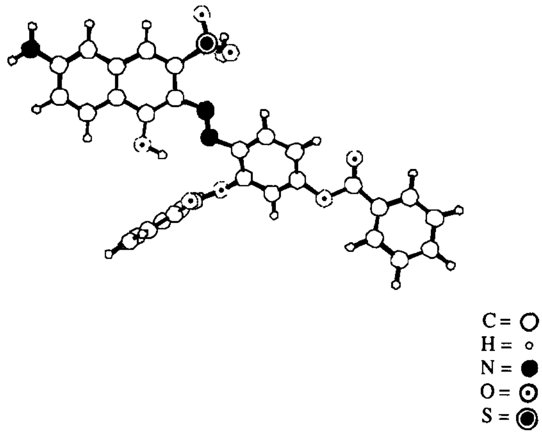


Fig. 1. Optimized structure of dye **6**.

The above facts can be explained taking into account the different structures of the two protein fibres.[14] The more extended linear structure of dye **6** seems to fit better to the helical chains of wool, while dyes **7** and **11**, for which a structure folded at the C=O group could be proposed (Fig. 2), fit the pleated sheets of silk better.

From this and previous work,[1] the following conclusions can be drawn:

—specific structures in the series must be developed not only for cotton and protein fibres, but also for each of the two protein fibres (silk and wool);

—a chemometric approach to QSAR, through statistical design of the more informative molecules and PLS modelling, can give valuable information, with a minimum number of compounds to be synthesized and tested.

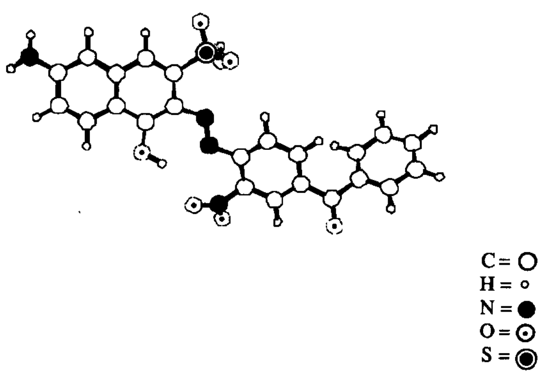


Fig. 2. Optimized structure of dye **11**.

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