Dyes and Pigments, Vol. 37, No. 2, pp. 187–196, 1998
© 1998 Elsevier Science Ltd. All rights reserved
Printed in Great Britain
PII: S0143-7208(97)00054-5
0143-7208/98 $19.00+0.00

Structure Optimization in a Series of Thiadiazole Disperse Dyes using a Chemometric Approach

M. Rita De Giorgi,[a]* Rosarina Carpignano[b] & Ado Cerniani[a]

[a]Dipartimento di Scienze Chimiche, Università di Cagliari, Via Ospedale 72,
09124 Cagliari, Italy
[b]Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino,
C.so M. D'Azeglio 48, 10125 Torino, Italy

(Received 21 April 1997; accepted 28 May 1997)

ABSTRACT

Structure optimization in a series of thiadiazolyl azo dyes to be used as disperse dyes for polyester fibres has been carried out by a chemometric approach based on experimental design in principal properties and PLS modelling. The thiadiazole nucleus confers a general excellent performance with respect to wet fastness. Light fastness depends on the substitution pattern. Three dyes with especially high fastness values have been identified. © 1998 Elsevier Science Ltd

Keywords: thiadiazole azo dyes, disperse dyes, structure optimization, polyester, chemometric approach.

INTRODUCTION

Heterocyclic disperse dyes are gaining increasing importance owing to their brightness and clarity of hue in comparison with aminoazobenzene disperse dyes.

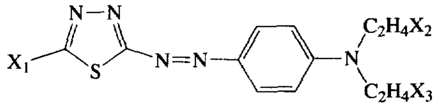
Disperse azo dyes derived from thiadiazole are of interest since they are suitable for dyeing various fibres [1, 2]. In a previous work [2] the affinity and fastness for polyester parameters were pointed out.

The fastness properties of a series of thiadiazolyl azo dyes, applied as disperse dyes on polyester fibres, have been explored previously by a chemometric approach with the aim of establishing quantitative structure–activity relationships (QSAR) [3, 4]. A small set of representative dyes of general

---

*Corresponding author.

formula I was selected by the technique of experimental design in principal properties [4]. This approach has shown to be a valid strategy for selecting the most informative structures in various series of dyes [4–7].



(I)

X_1 = common aromatic substituents;
X_2,X_3 = H, OH, CN.

The principal properties (PPs) developed by Skagerberg *et al.* [8], were used to describe the substituents at X_1. They are linear combinations of the traditional substituent descriptors (π, MR, σ_m, σ_p, and Verloop parameters L and B_1–B_4), obtained by principal component analysis (PCA). They have an interesting property in that they are orthogonal, and can thus be used as design variables in statistical designs for the selection of representative sets for QSAR.

Three PPs have been calculated for each substituent [8], but, only the two first PPs were used for the design, taking into account that they describe the main part of the variance in the data set. With two PPs, it is possible to define a two level factorial design in two variables, geometrically represented by a square, on which the substituents can be projected. The best substituents can be selected among those nearest each vertex of the square.

The following substituents were chosen for X_1 substitution:

PP1	PP2	Substituent
–	–	Cl
+	–	$NHCOC_6H_5$
–	+	H
+	+	C_6H_5

For X_2 and X_3 positions the substituents themselves were used as design variables

$$X_2: H = (-), CN = (+)$$
$$X_3: H = (-), CN = (+), OH = (0).$$

By a fractional factorial design in four variables, eight dyes were selected for the synthesis. Their wet and light fastenesses were measured on polyester fibres and a quantitative relationship between light fastness and structure was established by partial least squares (PLS) method. The PLS model was successively used to predict the fastness of new dyes, among which some have been synthesized and the corresponding fastnesses measured. The experimental values were generally in good agreement with the predicted values, except for two dyes bearing a CF_3 substituent at the X_1 position, which showed significantly higher values than predicted.

The CF_3 substituent belongs to the same group as far as only the two first PPs are concerned (- -), but differs from Cl in the sign of the third PP. The first PP is mainly related to sterical bulk and hydrophobicity, while the second PP encodes electronic aspects of the substituents. The third PP takes into account the shape of the substituent [8].

In order to verify if this structural feature is important in determining light fastness of the dyes a more complete study on this series of dyes was carried out.

PROCEDURES

Design of the training set

For the X_1 position (general formula I), the three PPs by Skagerberg [8], scaled to vary from -1 to $+1$, have been used as design variables. Three variables define a two level factorial design, geometrically represented by a cube. By plotting the PPs of the substituents on the cube, the ensemble of points obtained, each of them representing a substituent, can be distributed in eight groups. As the PPs are discrete variables, it is not possible to select substituents exactly at the vertices of the cube as the runs in factorial designs. The best substituents are selected in each group among those nearest to each vertex, taking into account also the difficulty of the synthesis.

The substituents selected for X_1 position are listed in Table 1.

For the X_2 and X_3 positions, on the basis of the results of previous works [3, 4], only H and CN were taken into account. Each of these positions was considered a two level variable, with $H=(-)$ and $CN=(+)$. A 2^{5-2} fractional factorial design allowed the selection of eight dyes, according to the matrix in Table 2.

Three of the selected dyes (**1**, **3**, **8**) were included in the series previously studied [4]; the other five were synthesized and their wet and light fastnesses measured.

TABLE 1
Substituent Selected for X_1 Position

PP1	*PP2*	*PP3*	*Substituent*
–	–	–	Cl
+	–	–	$NHCOC_6H_5$
–	+	–	H
+	+	–	SC_3H_7
–	–	+	Br
+	–	+	COC_6H_5
–	+	+	CH_3
+	+	+	C_6H_5

TABLE 2
Matrix of the Fractional Factorial Design and Corresponding Selected Dyes

	X_1								
Run	*PP1*	*PP2*	*PP3*	X_2	X_3	*Dye*	X_1	X_2	X_3
1	−	−	−	+	+	1	Cl	CN	CN
2	+	−	−	−	−	2	$NHCOC_6H_5$	H	H
3	−	+	−	−	+	3	H	H	CN
4	+	+	−	+	−	4	SC_3H_7	CN	H
5	−	−	+	+	−	5	Br	CN	H
6	+	−	+	−	+	6	COC_6H_5	H	CN
7	−	+	+	−	−	7	CH_3	H	H
8	+	+	+	+	+	8	C_6H_5	CN	CN

DATA ANALYSIS AND STRUCTURE DESCIPTION

PLS analysis was used to model fastness data as a function of the structure. PLS is a regression method based on PCA, aimed at detecting cause–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 [9,10].

The structure was described using the PPs [8] of the substituents at each position. The corresponding values are listed in Table 3.

EXPERIMENTAL

Intermediates

Preparation of 2-amino-5-benzamido-1,3,4-thiadiazole and 2-amino-5-phenyl-1,3,4-thiadiazole have been reported previously [4].

TABLE 3
Substituent Descriptor Values

Substituent	*PP1*	*PP2*	*PP3*
Cl	−0.592	−0.115°	−0.040
$NHCOC_6H_5$	0.875	−0.068	−0.353
H	−1.000	0.612	−0.480
SC_3H_7	0.278	0.090	−0.019
Br	−0.479	−0.195	0.057
COC_6H_5	0.044	−0.500	0.842
CH_3	−0.636	0.519	0.003
C_6H_5	0.364	0.008	0.170
CN	−0.569	−0.503	−0.663
CF_3[a]	−0.611	−0.404	0.327

[a] Substituent present in test set dyes.

2-Amino-5-bromo-1,3,4-thiadiazole was obtained by bromination [11] of 2-amino-1,3,4-thiadiazole at 40°C. The mixture was stirred for 2 days at 25°C and then concentrated *in vacuo*. The residue was poured into ice water and treated with 25% ammonia. The product was recrystallized from ethanol (mp 193–194°C).

2-Amino-5-chloro-1,3,4-thiadiazole was prepared by substitution of the bromine atom of 2-amino-5-bromo-1,3,4-thiadiazole with hydrochloric acid [11]. The product was recrystallized from ethanol (mp 191–192°C).

2-Amino-5-benzoyl-1,3,4-thiadiazole was prepared [12] by adding a cooled solution of thiosemicarbazide to a cooled and stirred solution of phenylglyoxal hydrate. The product obtained, recrystallized from ethanol (mp 171–172°C), was suspended in water, and ferric chloride added. The mixture was heated for 1 h and, after cooling, the precipitate was collected and crystallized from ethanol (mp 195–197°C).

2-Amino-5-propylthio-1,3,4-thiadiazole was prepared [13] by adding 0.07 mol of propyl iodide to 0.07 mol of 2-amino-1,3,4-thiadiazole dissolved in alcoholic KOH. The mixture was refluxed for 2 h, concentrated *in vacuo* and diluted with water. The product was recrystallized from benzene (mp 114–115°C).

2-Amino-1,3,4-thiadiazole, 2-amino-5-methyl-1,3,4-thiadiazole and 2-amino-5-trifluoromethyl-1,3,4-thiadiazole were commercial products (Aldrich).

Dye synthesis

The dyes were synthesized by diazotization of the corresponding amine with nitrosylsulfuric acid and subsequent coupling with the chosen coupling agent. The nitrosylsulfuric acid, prepared by adding 0.76 g of sodium nitrite to 5 ml of sulfuric acid, was cooled to 0°C and 0.01 mol of the various amines were added portionwise under stirring. Then 10 ml of a propionic–acetic acid mixture (1:4) were added to the diazonium salt keeping the temperature at 0–5°C for 2 h.

The clear diazonium solution obtained was added under stirring at 5°C, to a solution of 0.01 mol of the chosen coupling agent, dissolved in 20 ml of a 1:4 mixture of propionic–acetic acid, at pH 4, by adding sodium acetate portionwise. After a short time the reaction mixture was poured into iced water and filtered. The dyes obtained were washed with water on the filter, dried and recrystallized.

In Table 4 physical and spectroscopic data in *N*,*N*-dimethylformamide of the dyes are reported.

Dyeing of polyester

The polyester samples were dyed in a thermostatted bath (Linitest) with a 40:1 liquor ratio, at 120°C for 1 h (0.3% dye, 0.25% Na_2SO_4, 0.5% Disper-

TABLE 4
Physical and Spectroscopic Data of the Dyes

Dye	*Crystallization solvent*	*mp (°C)*	λ_{max} *(nm)*	*log* ε
1	Chlorobenzene	234–236	519	4.65
2	Chlorobenzene	241–242	525	4.55
3	Ethanol	142–143	488	4.61
4	Ethanol	113–116	505	4.63
5	Propanol	180–181	507	4.55
6	Ethanol:water (1:1)	184–185	512	4.70
7	Ligroine	172–173	500	4.52
8	Chlorobenzene	257–258	496	4.62
9[a]	Ethanol:water (1:1)	187–188	530	4.65
10[a]	Ethanol:water	201–202	522	4.64
11[a]	Propanol	214–215	507	4.60

[a] Dyes of the test set.

sogen A, 40% Lenol A on the weight of fibre. Dispersogen A and Lenol A were Hoechst products).

Fastness assessment

Fastness to light, to washing and to perspiration were measured according to standard procedures [14]. The fastness data are listed in Table 5.

Calculations

PCA and PLS analysis were carried out on a Compaq 4/66 computer using the SIMCA-3B package developed by S. Wold and coworkers at the University of Umea (Sweden).

RESULTS AND DISCUSSION

PLS model

A preliminary PCA analysis was done on the structure descriptors of the training set dyes (9×8 data set matrix). A four component model was obtained explaining about 90% of the variance in the data (30% with the first component, 47.9% with two components and 76.5% with three components). The representation of the training set in the PCA space in Fig. 1 shows that the selected dyes span the experimental dominion in a fairly good way.

Light fastness showed a fairly high variability along the series and was modelled as a function of the structure. Fastness to washing and to

TABLE 5
Fastness Values of the Selected Dyes

Dye	*Fastness*					
	Washing			*Perspiration*		*Light*
	Mild	*Medium*	*Strong*	*Acid*	*Alkaline*	
1	5	4–5	4	5	5	7
2	5	5	4–5	5	5	4
3	5	5	5	5	5	7
4	5	5	4–5	5	5	5
5	5	5	5	5	5	7
6	5	5	5	5	5	7–8
7	5	5	5	5	5	6
8	5	5	5	5	5	5–6

perspiration were not modelled because they were generally excellent, with scores near the top of the scale.

Light fastness values, y, (Table 5) were modelled by a three component model explaining about 89% of the y variance. The results of the PLS analysis are reported in Table 6.

The most important variables (highest modelling power values) appear to be the PPs of X_2 and X_3 substituents, i.e. the substituents at the diethylamino group; a minor effect is provided by PP1 of the X_l substituents.

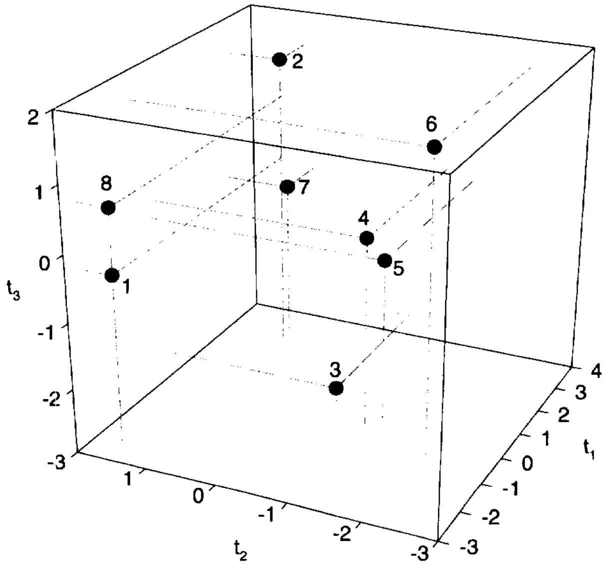


Fig. 1. Representation of the training set in the PCA space.

TABLE 6
Variable Loadings *p* and Corresponding Modelling Powers Ψ for each Component of the PLS Model

	p1	*Ψ1*	*p2*	*Ψ2*	*p3*	*Ψ3*
y variable	1	0.32	1	0.50	1	0.67
x variables						
X_1-PP1	−0.25	0.04	−0.41	0.27	−0.32	0.31
PP2	−0.15	0	0.24	0	−0.03	0
PP3	0.22	0.02	−0.01	0	0.27	0
X_2-PP1	0.19	0	−0.50	0.36	0.45	0.63
PP2	−0.19	0	0.50	0.36	−0.45	0.63
PP3	−0.19	0	0.50	0.36	−0.45	0.63
X_3-PP1	0.50	0.66	−0.10	0.68	−0.26	0.98
PP2	−0.50	0.66	0.10	0.68	0.26	0.98
PP3	−0.50	0.66	0.10	0.68	0.26	0.98
Variance explained (%)	54.0		74.6		89.4	

TABLE 7
Calculated Values of Light Fastness and Residuals

Dye	*Light fastness*	
	Calculated	Δ
1	6.9	0.1
2	3.7	0.3
3	6.8	0.2
4	5.5	−0.5
5	6.9	0.1
6	7.2	0.3
7	6.3	−0.3
8	5.6	−0.1

The PLS model was used to recalculate the lightfastness values of the training set dyes. The calculated values, listed in Table 7, show a good agreement with the experimental ones.

The PLS model was successively used to predict the fastness values of dyes not included in the training set.

TABLE 8
Structures and Fastness Values of the Predicted Dyes

Dye	*Structure*			*Fastness to washing*			*Fastness to light*		
	X_1	X_2	X_3	*Mild*	*Medium*	*Strong*	*Exp.*	*Pred.*	Δ
9	CF_3	H	H	5	5	5	7	7.1	−0.1
10	CF_3	H	CN	5	5	5	7–8	7.6	−0.1
11	CF_3	CN	CN	5	5	5	8	7.8	0.2

Three dyes with a CF_3 substituent at X_1 position were examined (Table 8); two of them (dyes **10**, **11**) were in the prediction set of the series previously studied, the third (dye **9**) was synthesized and measured. The low values of the residuals show that the PLS model established has a satisfactory predictive capability, also for dyes with the CF_3 substituent.

CONCLUSIONS

Structure optimization in a series of thiadiazole azo disperse dyes has been carried out by a chemometric approach based on experimental design in principal properties and PLS modelling.

The work has shown the importance of using three, instead of two, PPs of the substituents as variables for designing the training set in order to establish a PLS model with satisfactory predictive capability.

This present and previous studies have shown that azo disperse dyes bearing the thiadiazol moiety group exhibit a generally excellent performance to wet fastness on polyester fibres.

On the contrary, fastness to light depends on the substitution pattern. Substitution at the diethylamino group (X_2 and X_3 positions) is the most important feature affecting lightfastness with a strong positive effect of the CN substituent. Substitution on the thiadiazole group (X_1) shows the neat positive effect with C_6H_5CO and CF_3 substituents.

Three dyes (**6**, **10**, **11**) with fastness values not often achieved have been identified.

ACKNOWLEDGEMENT

This work was supported by CNR and MURST, Rome.

REFERENCES

1. De Giorgi, M. R. and Cerniani, A., *Melliand Textilber.*, 1992, **73**, 433.
2. Arcoria, A., De Giorgi, M. R., Fatuzzo, F. and Longo, M. L., *Dyes and Pigments*, 1993, **21**, 67.
3. De Giorgi, M. R., Carpignano, R. and Viscardi, G., *Melliand Textilber.*, 1993, **74**, 234.
4. De Giorgi, M. R., Carpignano, R., Cerniani, A. and Cesare, F., *Ann. Chim.*, 1995, **85**, 543.
5. De Giorgi, M. R., Cerniani, A., Carpignano, R. and Savarino, P., *J. Soc. Dyers Colour.*, 1993, **109**, 405.

6. De Giorgi, M. R., Carpignano, R. and Scano, P., *Dyes and Pigments*, 1994, **26**, 175.
7. De Giorgi, M. R. and Carpignano, R., *Dyes and Pigments*, 1996, **30**, 79.
8. Skagerberg, B., Bonelli, D., Clementi, S., Cruciani, G. and Ebert, C., *Quant. Struct. -Act. Relat.*, 1989, **8**, 32.
9. Wold, S., Albano, C., Dunn III, A. J., Esbensen, K., Hellberg, S., Johansson, E. and Sjostrom, M., *Chemometrics*, ed. B. R. Kowalski. Reidel, Dordrecht, 1984, p. 17.
10. Carpignano, R., Savarino, P. and Barni, E., *Dyes and Pigments*, 1985, **6**, 189.
11. Rathgeb, P., *S. African P. 718,390, C.A.*, 1973, **78**, 84417.
12. Werber, G., Buccheri, F. and Marino, M. L., *J. Heterocyclic Chem.*, 1975, **12**, 581.
13. Pala, J., *Farmaco*, 1958, **13**, 660.
14. The Society of Dyers and Colourists, *Methods of Test for Colour Fastness of Textiles and Leather*, 4th edn., Bradford, 1978.