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The Synthesis of Disperse and Cationic Dyes from Acid Dye Structures

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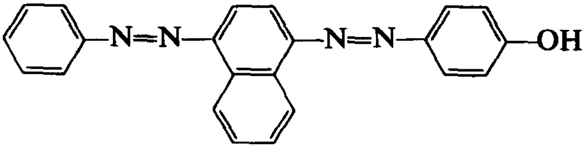
ABSTRACT

This paper is concerned with the conversion of some mono- and di-sulfonated naphthol azo dyes to disperse dyes suitable for poly(ethyleneterephthalate) fibers, and cationic dyes for cationic dyeable polyester and acrylic fibers. The chemical structure of these new dyes has been confirmed by ^{1}*H-NMR, FAB or DCI mass spectrometry, and in some cases by elemental analysis. Some fastness properties and absorption spectral data of both types of dyes are also reported, as well as an interesting limitation in the naphthalene-based acid dyes suitable for the described conversion.*

INTRODUCTION

The chemical literature contains few examples of disperse or cationic dyes based on the naphthalene ring system, even though there are numerous examples of acid and direct dyes containing one or more naphthalene rings. Among the examples of commercial naphthalene-based disperse dyes is compound **1**. This dye is typical of the lightfast azo disperse dyes made from



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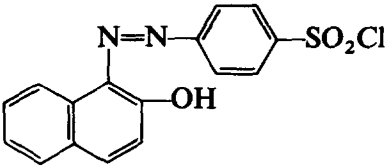
Dyes and Pigments 0143-7208/90/$03·50



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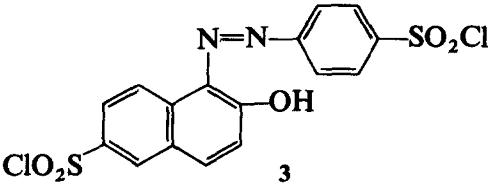

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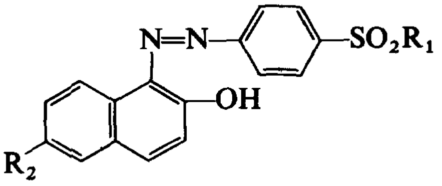
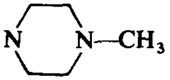
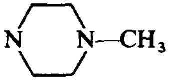
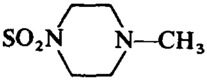
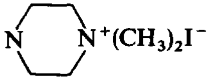
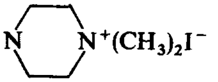
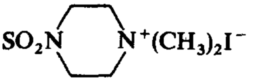


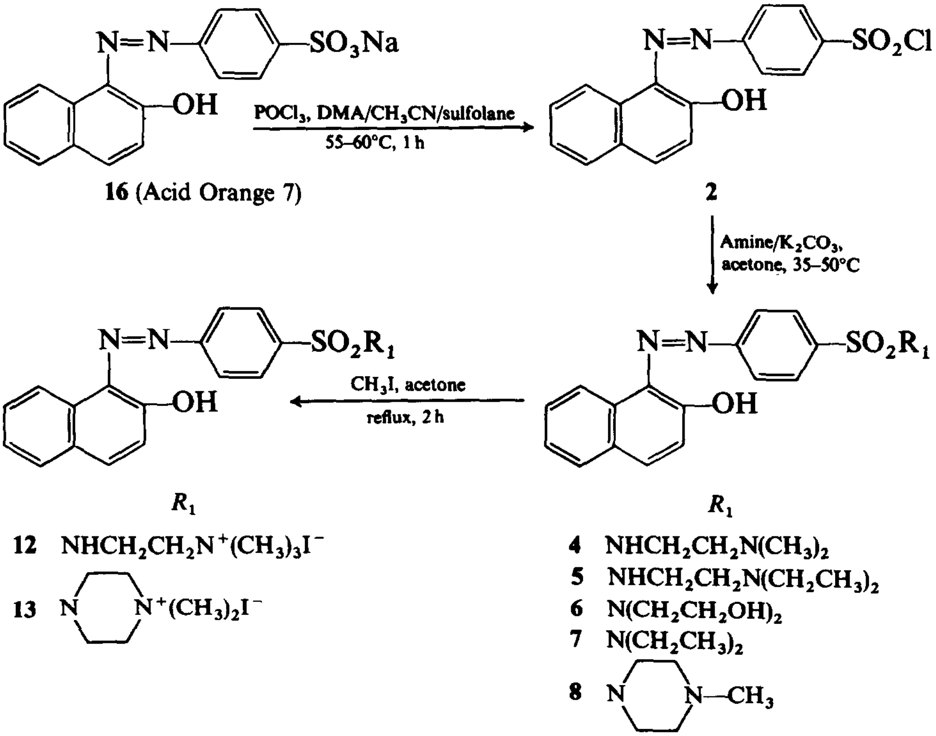
Compound	R_1	R_2
4	$NHCH_2CH_2N(CH_3)_2$	H
5	$NHCH_2CH_2N(CH_2CH_3)_2$	H
6	$N(CH_2CH_2OH)_2$	H
7	$N(CH_2CH_3)_2$	H
8		H
9	$NHCH_2CH_2N(CH_3)_2$	$SO_2NHCH_2CH_2N(CH_3)_2$
10	$N(CH_2CH_3)_2$	$SO_2N(CH_2CH_3)_2$
11		
12	$NHCH_2CH_2N^+(CH_3)_3I^-$	H
13		H
14	$NHCH_2CH_2N^+(CH_3)_3I^-$	$SO_2NHCH_2CH_2N^+(CH_3)_3I^-$
15		

a phenol coupler that do not have particularly good sublimation fastness. Some relatively recent papers by Fujita[1,2] described the efficient conversion of the sodium sulfonate group of certain pyrazolone and naphthol azo dyes to the corresponding chlorosulfonyl group to give compounds that are precursors of dyes for use in instant photography. This suggested that one should be able to utilize some well-known and commercially used acid dyes to prepare and evaluate naphthalene-based azo disperse and cationic dyes containing one or more aminoalkyl sulfonamide groups.

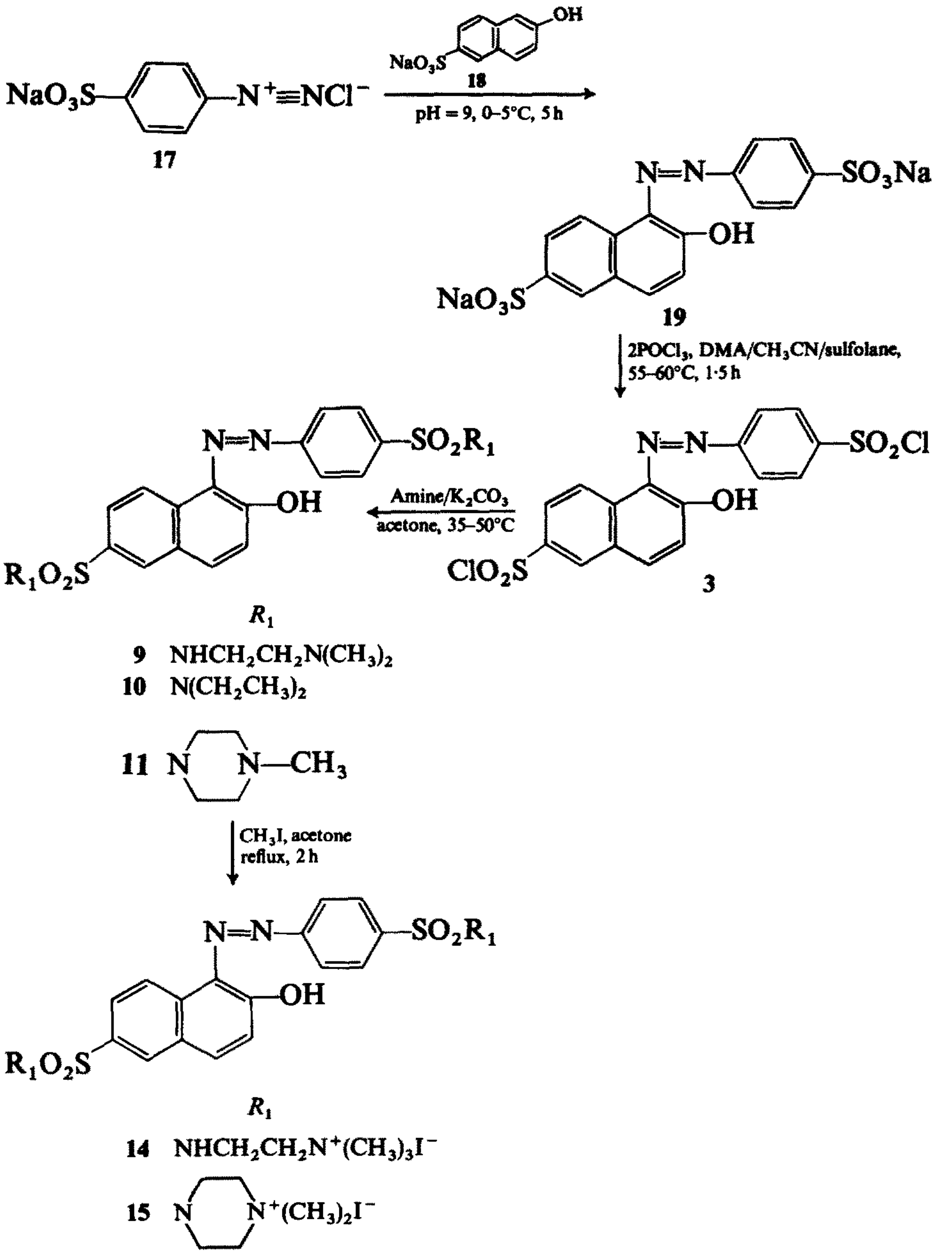
We anticipated that the condensation of chlorosulfonyl group-containing azo dyes with various amines[3–9] would provide an effective way to make disperse dyes having good sublimation fastness, and that these newly formed disperse dyes would be readily converted to cationic dyes having good fastness properties as well. To examine the feasibility of this idea, compounds **2** and **3** were synthesized from the acid dyes formed by coupling sulfanilic acid to β-naphthol and Schaeffer's acid. These two intermediates were then used to prepare disperse dyes **4–11** and cationic dyes **12–15**.

RESULTS AND DISCUSSION

The reaction sequences used to prepare dyes **4–11** and **12–15** are shown in Schemes 1 and 2. The treatment of the corresponding acid dyes (sodium sulfonates) **16** and **19** with phosphoryl chloride in dimethylacetamide (DMA)–acetonitrile-sulfolane[1,2] afforded the desired sulfonyl chlorides **2** and **3** in 82–90% yields of isolated products. The progress of these reactions was followed by TLC using EtOAc/HOAc/H_2O (80:20:15) as the eluent, and the structure of the sulfonyl chlorides (**2** and **3**) was confirmed by elemental analysis. The latter results and melting points are given in Table 1.



Scheme 1. Reaction sequence used to prepare dyes **4–8** and **12–13**.



Scheme 2. Reaction sequence used to prepare dyes **9–11** and **14–15**.

TABLE 1
Elemental Analysis and Melting Point Data for Sulfonyl Chloride-Containing Compounds 2 and 3

Compound	*C (%)*		*H (%)*		*Cl (%)*		*M.p. (°C)*	*Yield (%)*
	Calcd	*Found*	*Calcd*	*Found*	*Calcd*	*Found*		
2	55·49	54·91	3·17	3·20	10·26	10·03	206–208	90
3	43·15	43·06	2·26	2·24	15·92	15·90	244–246	82

The synthesis of sulfonyl chloride **3** also required the preparation of acid dye **19** which was obtained by conventional diazotization of sulfanilic acid[10] and coupling reaction of the resulting diazonium salt **17** with Schaeffer's acid **18**[11] (cf. Scheme 2).

The next stage of the synthesis of the sulfonamide group-containing dyes **4–11** involved the condensation of certain amines (*N*,*N*-dimethylethylenediamine, *N*,*N*-diethylethylenediamine, diethylamine, diethanolamine, and *N*-methylpiperazine) with the sulfonyl chlorides **2–3**. The reaction was carried out in acetone[12] at 35–50°C for 2–7 h, depending on the amine used, and K_2CO_3 was used as the acid acceptor. The progress of each reaction was followed by TLC (silica gel) using either EtOAc/HOAc/H_2O (80:20:15) or BuOH/EtOH/NH_4OH/pyridine (4:1:3:2) as the eluent. These reactions produced the disperse dyes in 50–90% yields of purified product.

The treatment of disperse dyes **4**, **8**, **9** and **11** with a 20% excess of methyl iodide in boiling acetone gave the cationic dyes **12–15** in 75–96% yield. The progress of the formation of quaternary salts was followed by TLC using either EtOAc/HOAc/H_2O (80:20:15) or BuOH/EtOH/NH_4OH/pyridine (4:1:3:2) as the eluent. The chemical structures of dyes **4–15** were established by ^{1}H-NMR spectroscopy (Table 2) and FAB (fast atom bombardment) or DCI (desorption chemical ionization) mass spectrometry (Table 3). In some cases elemental analysis was also performed.

The data obtained from recording visible spectra of the dyes **4–15** are reported in Table 4. These data show that the type of substituted amine does not affect the position of λ_{max} and that the new dyes have the same λ_{max} value as the acid dyes used in their synthesis, as would be expected.

The results from the evaluation of the lightfastness and sublimation fastness of dyes **4–15** are given in Table 5. Although the new disperse dyes are not stable to a 40-h exposure to glass-filtered xenon arc light, their dry-heat stability is generally quite good. Only the two dyes containing just one sulfonamide linkage and derived from a secondary aliphatic amine (cf. **7** and **8**) did not possess good sublimation fastness. All three of the disperse dyes containing *two* sulfonamide linkages (**9–11**) were rated very high in this test.

TABLE 2

^{1}H-NMR Data Recorded on Dyes **4–15** Using TMS as the Internal Reference

Dye	*^{1}H-NMR [DMSO-d_6, δ(ppm), J(Hz)]*
4	δ 2·04 (s, 6H), δ 2·24 (t, 2H, *J* = 6·6), δ 2·84 (t, 2H, *J* = 6·4), δ 6·74 (d, 1H, *J* = 9·6), δ 7·44 (t, 1H, *J* = 6·8), δ 7·69 (t, 1H, *J* = 6·8), δ 7·75 (d, 1H, *J* = 6·8), δ 7·84–7·89 (m, 5H), δ 8·44 (d, 1H, *J* = 8·1), δ 16·16 (s, 1H)
5	δ 0·83 (t, 6H, *J* = 7·3), δ 2·30–2·35 (m, 6H), δ 2·78 (t, 2H, *J* = 6·6), δ 6·72 (d, 1H, *J* = 9·5), δ 7·44 (t, 1H, *J* = 7·8), δ 7·66 (t, 1H, *J* = 7·2), δ 7·85 (d, 1H, *J* = 8·7), δ 7·87–7·99 (m, 5H), δ 8·40 (d, 1H, *J* = 8·1), δ 16·11 (s, 1H)
6	δ 3·21 (t, 4H, *J* = 6·6), δ 3·52 (br s, 4H), δ 4·80 (br s, 2H), δ 6·76 (d, 1H, *J* = 9·5), δ 7·48 (t, 1H, *J* = 7·3), δ 7·71 (t, 1H, *J* = 8·1), δ 7·75 (d, 1H, *J* = 9·5), δ 7·94–7·97 (m, 5H), δ 8·50 (d, 1H, *J* = 8·1), δ 16·16 (s, 1H)
7[a]	δ 1·13 (t, 6H, *J* = 6·9), δ 3·24 (q, 4H, *J* = 6·9), δ 6·67 (d, 1H, *J* = 9·7), δ 7·39 (t, 1H, *J* = 6·9), δ 7·52 (t, 1H, *J* = 6·8), δ 7·64–7·67 (m, 5H), δ 7·83 (d, 1H, *J* = 8·8), δ 8·37 (d, 1H, *J* = 7·8), δ 16·11 (s, 1H)
8	δ 2·11 (s, 3H), δ 2·35 (s, 4H), δ 2·89 (s, 4H), δ 6·70 (d, 1H, *J* = 9·7), δ 7·43 (t, 1H, *J* = 7·8), δ 7·55 (t, 1H, *J* = 7·8), δ 7·68 (d, 1H, *J* = 7·8), δ 7·74–7·95 (m, 5H), δ 8·37 (d, 1H, *J* = 7·8), δ 15·72 (s, 1H)
9	δ 2·04 (s, 12H), δ 2·24 (t, 4H, *J* = 7·3), δ 2·86 (t, 4H, J = 7·3), δ 6·90 (d, 1H, *J* = 9·5), δ 7·90–8·21 (m, 7H), δ 8·68 (d, 1H, *J* = 8·8)
10	δ 1·03 (t, 12H, *J* = 6·9), δ 3·17 (q, 8H, *J* = 6·9), δ 6·74 (d, 1H, *J* = 8·7), δ 7·64–8·02 (m, 7H), δ 8·89 (d, 1H, *J* = 8·7)
11	δ 2·21 (s, 6H), δ 2·39 (br s, 8H), δ 2·88 (br s, 8H), δ 7·02 (d, 1H, *J* = 9·6), δ 7·87–8·37 (m, 7H), δ 8·72 (d, 1H, *J* = 8·6)
12	δ 3·08 (s, 9H), δ 3·38 (br s, 2H), δ 3·43 (t, 2H, *J* = 6·3), δ 6·74 (d, 1H, *J* = 8·9), δ 7·46 (t, 1H, *J* = 6·8), δ 7·58 (t, 1H, *J* = 6·8), δ 7·72 (d, 1H, *J* = 6·8), δ 7·97–8·00 (m 5H), δ 8·41 (d, 1H, *J* = 8·4)
13	δ 3·05 (s, 6H), δ 3·33 (br s, 4H), δ 3·43 (br s, 4H), δ 6·74 (d, 1H, *J* = 9·0), δ 7·47 (t, 1H, *J* = 7·5), δ 7·59 (t, 1H, *J* = 7·5), δ 7·70 (d, 1H, *J* = 7·5), δ 7·85 (d, 2H, *J* = 9·0), δ 7·94 (d, 1H, *J* = 9·9), δ 8·02 (d, 2H, *J* = 7·8), δ 8·41 (d, 1H, *J* = 8·1)
14	δ 3·09 (s, 18H), δ 3·25 (br s, 4H), δ 3·43 (br, s, 4H), δ 6·96 (d, 1H, *J* = 9·6), δ 7·93–8·27 (m, 7H), δ 8·41 (d, 1H, *J* = 8·7), δ 15·80 (s, 1H)
15	δ 3·10 (s, 12H), δ 3·25 (br s, 8H), δ 3·44 (br s, 8H), δ 6·97 (d, 1H, *J* = 8·7), δ 7·94–8·29 (m, 7H), δ 8·7 (d, 1H, *J* = 8·7), δ 15·83 (s, 1H)

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[a] The spectrum was recorded in $CDCl_3$ solution.

TABLE 3
Positive FAB and DCl Mass Spectrometric Data for Dyes **4**–**15**

Dye	*Mol. wt*	$[M+H]^+$ (%)[b]	$[M\text{-}I+H]^+$ (%)[b]	$[M\text{-}2I+H]^+$ (%)[b]
4[a]	398·47	399·1 (25)	—	—
3	426·52	427·1 (85)	—	—
6	415·45	416·1 (100)	—	—
7	383·45	384·0 (100)	—	—
8	410·48	411·0 (100)	—	—
9[a]	548·67	549·2 (100)	—	—
10	518·63	518·8 (100)	—	—
11	572·69	573·0 (92)	—	—
12	540·40	—	413·0 (45)	—
13	552·41	—	425·0 (48)	—
14	832·53	—	705·1 (100)	578·2 (88)
15	856·55	—	729·1 (7)	603·2 (22)

[a] For these dyes DCl mass spectra were recorded.
[b] Relative abundance.

However, this may be a consequence of the light shades resulting from low exhaustion. Like many heat-stable automotive disperse dyes, each of these new dyes has a molecular weight above 500. Interestingly, the presence of the NH group in dye **5** causes a significant improvement in sublimation fastness compared with dye **8** which has a comparable molecular weight.

The lightfastness of the cationic dyes **12**–**15** on acrylic fibers (as might be expected) is significantly better than that observed on cationic dyeable

TABLE 4
Visible Spectra[a] of Dyes **4**–**15**

Dye	λ_{max} *(nm)*	$\varepsilon \times 10^4$ *(l/mole.cm)*
4	482	1·90
5	482	2·00
6	482	2·50
7	482	2·79
8	482	2·11
9	476	1·79
10	476	2·10
11	476	2·15
12	482	2·16
13	482	2·11
14	476	2·16
15	476	2·65

[a] The spectra were recorded in 95% EtOH.

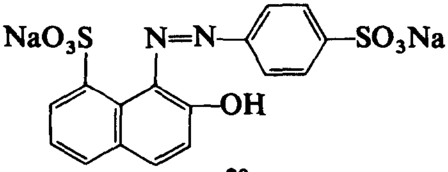
TABLE 5
Lightfastness and Dry-Heat Treatment Testing Results[a]

Dye	*Lightfastness*			*Dry-heat treatment (177 ± 2°C, 30 s)*						
	Polyester	*Modified polyester*	*Poly-acrylonitrile*	*Wool*	*Poly-acrylonitrile*	*Polyester*	*Nylon*	*Cotton*	*Acetate*	*Change of color*
4	2–3			4	4	4	4	4	4	5
5	2–3			4–5	4–5	4–5	4–5	4–5	4–5	5
6	2			5	5	5	5	5	5	5
7	2			3–4	3–4	3	3	3–4	3–4	5
8	3			3–4	3–4	3	3	3–4	3–4	5
9	1			5	5	5	5	5	5	5
10	1–2			5	5	5	5	5	5	4–5
11	2			5	5	5	5	5	5	5
12		1–2	4							5
13		1–2	4–5							5
14		1–2	2–3							5
15		1	2							5

[a] All samples were rated on a scale of 1–5.

polyester, and it is quite good in the cases involving **12** and **13**, the two smaller dyes of this group (i.e. those derived from Acid Orange 7). The results of the dry-heat treatment (change of color) indicate that dyes **12** and **13** possess good all-around fastness properties on acrylic fibers.

It is also apparent from this work that the disperse and cationic dyes derived from C.I. Acid Orange 7 (and ultimately **2**) give much deeper shades on the fibers used in this study than the dyes synthesized from the bis(chlorosulfonyl)azo intermediate **3**, probably due to limitations in fiber accessibility. We wish to mention, too, that it was *not* possible to synthesize the corresponding bis(chlorosulfonyl)azo dye of **20** (an isomer of **19**).



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Elemental analysis and mass spectral data indicate that in this case the reaction stops at the monochlorosulfonyl intermediate. It seems that the presence of a peri group inhibits the conversion of the SO_3Na group attached to the naphthalene ring to the desired SO_2Cl group.

SUMMARY AND CONCLUSIONS

It has been shown that acid dyes containing a single sodium sulfonate group can be readily elaborated in good yields to other dye classes for synthetic fibers. In the present case, disperse dyes (cf. **4–8**) for polyester and acetate fibers, and cationic dyes (**11–12**) suitable for modified polyester and acrylic fibers, were obtained. It was also possible to extend work in this area to include acid dyes containing two sodium sulfonate groups as long as neither of the SO_3Na groups was peri to a bulky substituent (a phenylazo group in our experiments). However, the bis(sulfonamido) dyes (**9–11** and **14–15**) give unsatisfactory (40–50%) exhaustion and, consequently, appreciably weaker shades on the fibers employed. It is important to note that the bis(aminoalkylsulfonamide)-type disperse and cationic dyes exhibited lower percentage exhaustion and lower lightfastness. In the case of dye **9**, too high a water solubility was probably the major reason for the observed low exhaustion.

Like many cationic dyes, **12** and **13** possess good light stability at 40 h when applied to polyacrylonitrile fibers rather than to cationic-dyeable polyester. In addition, the conversion of dye **8** to dye **13** preserves the light stability (albeit modest) noted in the disperse dye.

EXPERIMENTAL

General

The chemicals used to synthesize the dyes were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA) and were used without further purification. The purity of the resulting sulfonyl chlorides and dyes was checked by TLC using glass-backed silica gel 60 plates from Bodman Chemical Co. (Doraville, GA, USA) and the structures were confirmed by ^{1}H-NMR, FAB and/or DCI mass spectrometry, and by elemental analysis. The ^{1}H-NMR spectra were recorded at 300 MHz with a GN spectrometer in DMSO-d_6 or $CDCl_3$ using TMS as the internal standard. The mass spectrometric analyses employed a JEOL (Tokyo, Japan) HX 110 HF double-focusing mass spectrometer equipped with FAB or DCI ionization sources. The FAB experiments utilized nitrobenzyl alcohol as the matrix, whereas in the DCI experiments isobutane was used as the reagent gas. The visible spectra were recorded using a Perkin–Elmer R-24A spectrophotometer. Microanalyses were performed by Atlantic Microlab. Inc. (Norcross, GA, USA). Melting points were determined on a Mel-Temp. capillary melting point apparatus and are uncorrected.

Application of disperse dyes to polyester fabric[13]

Polyester fabric was dyed at 130°C for 1·5 h on an Ahiba Polymat (type PN) dyeing machine using a dyebath containing 2% of the dye and 4% of dispersing agent (Irgasol DA PDR) based on the fabric weight (liquor ratio = 1:25, pH = 5·5).

Application of cationic dyes to modified polyester[14] (Dacron 64)

Modified polyester was dyed at 120°C for 1·5 h on an Ahiba Polymat (type PN) dyeing machine using a dye bath containing 2% of the dye and 10% of anhydrous Na_2SO_4 based on the fabric weight (liquor ratio 1:25, pH = 4·5).

Application of cationic dyes to polyacrylonitrile fabric[15] (Orlon)

Polyacrylonitrile fabric (Orlon) was dyed at 100°C for 1 h on an Ahiba Texomat dyeing machine using a dye bath containing 2% of dye, 10% of anhydrous Na_2SO_4, and 2% of retarder (Basacryl® Salt NB-K4) (BASF) based on the fabric weight (liquor ratio 1:25, pH = 4·5).

Lightfastness and dry-heat treatment

The lightfastness of the dyes was recorded on a Xenotest 1200 apparatus (Original Hanau) using the chamber conditions of AATCC Test Method 16E-1982.[16] The test conditions were:

Black panel temperature	63°C
Relative humidity	30%
Chamber temperature	50°C
Window glass filters	310 nm cut-off
Duration of test	40 h

The samples were rated with the aid of the gray scale for color change.

Fastness to dry-heat treatment was measured with an Atlas Scorch Tester at 177 ± 2°C (30 s) according to AATCC Test Method 177–1984.[17] The change of color was evaluated using the gray scale for color change and the staining of the undyed fabrics was evaluated using the AATCC Chromatic Transference Scale.

Synthesis of dyes and intermediates

*Synthesis of the acid dye **19***

Sulfanilic acid (17·9 g, 0·10 mol) was dissolved in water (100 ml) with Na_2CO_3 (6 g, 0·056 mol) at 40°C. The solution was cooled to 20°C and 30% HCl (30 ml, 0·30 mol) was added. After cooling this suspension to 0°C, 4N-$NaNO_2$ (25 ml, 0·10 mol) was added. Diazotization was then effected over the next 30 min.

Schaeffer's acid sodium salt (**18**, 29·5 g, 0·12 mol) was dissolved in water (150 ml) containing Na_2CO_3 (10 g, 0·09 mol). The solution was cooled to 0°C and Na_2CO_3 (30 g, 0·28 mol) was added. To this solution the diazonium salt **17** was added dropwise at 0–5°C. The coupling reaction was carried out for 5 h. At this point the dye was salted out of solution by adding NaCl. Yield: 93·45%. TLC: $R_f = 0{\cdot}38$ (BuOH/EtOH/NH_4OH/pyridine, 4:1:3:2). Mass spectrum (*m/e*): 407 (45%) $[M - Na]^-$, 429 (42%) $[M - 2Na + H]^-$.

*Synthesis of sulfonyl chlorides **2** and **3***

To a stirred suspension of the sodium salt of Orange II (**16**, 7·0 g, 0·020 mol) in acetonitrile (20 ml), sulfolane (20 ml) and DMA (7·2 ml), was added (dropwise) $POCl_3$ (7·2 ml, 0·078 mol) over 10 min without exceeding a reaction temperature of 40°C. The reaction mixture was then stirred at 55–60°C for 1 h, cooled to room temperature, and the product collected by filtration. The sulfonyl chloride was washed with cold water and air-dried. Additional product was obtained by adding cold water to the filtrate. The two crops of **2** had m.pt 206–208°C, total yield 6·25 g (90%).

The sulfonyl chloride **3** was obtained in 82% yield by increasing the reaction time to 1·5 h and the amount of $POCl_3$ used by 100%.

Synthesis of sulphonamide disperse dye 4

To a solution of *N,N*-dimethylethylenediamine (1·53 g, 0·017 mol) in dry acetone (30 ml), K_2CO_3 (4·8 g, 0·035 mol) and a suspension of sulfonyl chloride **2** (6 g, 0·017 mol) in dry acetone (100 ml) were added. The reaction mixture was stirred at 35–40°C for 2 h, cooled to room temperature, poured into water, and extracted with EtOAc. After concentrating the extract, 6·4 g (80·4%) of dye **4** were obtained, m.pt 166°C. TLC: $R_f = 0{\cdot}31$ (EtOAc/HOAc/H_2O, 80:20:15).

Analysis for $C_{20}H_{22}O_3N_4S$: Calcd: C, 60·3; H, 5·5; N, 14·1. Found: C, 60·2; H, 5·6; N, 14·0%.

The remaining disperse dyes (**5**–**11**) were prepared using the procedure described for **4**, but the method of their isolation from the reaction mixture was sometimes different.

Synthesis of dye 5

At the end of the reaction period, K_2CO_3 was removed by filtration and the filtrate was evaporated to one-third the volume. The dye then crystallized from solution on standing. Yield 76·3%, m.pt 130–132°C. TLC: $R_f = 0{\cdot}44$ (EtOAc/HOAc/H_2O, 80:20:15).

Synthesis of Dyes 6, 7 and 10

The reaction was carried out for 5 h (dyes **6** and **7**) and 7 h (dye **10**). Afterwards the mixture of product and K_2CO_3 was collected by filtration, digested with EtOAc (100 ml), and filtered again. The filtrate was evaporated to one-third the volume to facilitate precipitation of the dye.

Dye **6**: Yield 51·4%, m.pt 178°C. TLC: $R_f = 0{\cdot}84$ (BuOH/EtOH/NH_4OH/pyridine, 4:1:3:2).

Dye **7**: Yield 72·2%, m.pt 187°C. TLC: $R_f = 0{\cdot}92$ (EtOAc/HOAc/H_2O, 80:20:15).

Dye **10**: Yield 80·0%, m.pt 170–172°C. $R_f = 0{\cdot}94$ (BuOH/EtOH/NH_4OH/pyridine, 4:1:3:2).

Synthesis of 8, 9 and 11

After the reaction the product and K_2CO_3 mixture was collected, the solid was stirred with water, filtered again, and washed with water until the pH of the filtrate tested neutral to Brilliant Yellow test paper.

Dye **8**: Yield 90·2%, m.pt 170–172°C. TLC: $R_f = 0{\cdot}68$ (EtOAc/HOAc/H_2O, 80:20:14).

Dye **9**: Yield 49·3%, m.pt 168–170°C. TLC: $R_f = 0{\cdot}12$ (EtOAc/HOAc/H_2O, 80:20:15).

Dye **11**: Yield 85·0%, m.pt 299°C. TLC: $R_f = 0{\cdot}32$ (BuOH/EtOH/NH_4OH/pyridine, 4:1:3:2).

Synthesis of cationic dye 12

Dye **4** (2 g, 0·005 mol) was dissolved in acetone (50 ml) and to the solution methyl iodide (0·85 g, 0·006 mol) was added. The reaction was stirred under reflux for 2 h and after this time the precipitated product was collected. This gave 2·6 g of the dye **12**, 96·0%, m.pt = 252–254°C. TLC: $R_f = 0{\cdot}24$ (EtOAc/HOAc/H_2O, 80:20:15).

Analysis for $C_{21}H_{25}O_3N_4SI$. Calcd: C, 46·7; H, 4·6; N, 10·4. Found: C, 46·8; H, 4·7; N, 10·35%.

Dyes **13–15** were synthesized using the procedure outlined above for **12**.

Dye **13**: Yield 89·4%, m.pt 222–224°C. TLC: $R_f = 0{\cdot}33$ (EtOAc/HOAc/H_2O, 80:20:15).

Dye **13**: Yield 75·9%, m.pt 194°C. TLC: $R_f = 0{\cdot}1$ (BuOH/EtOH/NH_4OH/pyridine, 4:1:3:2).

Dye **15**: Yield 80·8%, m.pt 266°C. TLC: $R_f = 0{\cdot}05$ (BuOH/EtOH/NH_4OH/pyridine, 4:1:3:2).

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