

## New Reactive Dyes Containing Fluorine Substituents in the Vinylsulfone Group

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### ABSTRACT

*New reactive dyes having good affinity for the fibre are obtained by introducing fluorine atoms into the vinylsulfone group of conventional reactive dyes. This new reactive centre for dyes which form a covalent link with the fibre is the  $\text{SO}_2\text{CF}=\text{CFCl}$  group. Interaction of 1,2-dichlorodifluoroethene with 4-N-methoxycarbonylaminothiophenol gives 4-N-methoxycarbonylaminothiophenyl(2-chloro-1,2-difluoroethenyl)sulfone. Diazotization and coupling gives azo dyes which colour polyamide fibres from an alkaline dye bath, with formation of a covalent linkage.*

### 1 INTRODUCTION

Typical reactive dyes which give a covalent link with the fibre are azo dyes containing labile chloro or fluoro substituents, as in, for example, triazine, pyrimidine and benzothiazole moieties. Thus, atoms in such dyes react with the cellulosic hydroxy groups or with the NH groups of polyamide fibre. Compounds containing the vinylsulfone substituent are also widely used.

Introduction of the fluorine group into the vinylsulfone group should increase the ability of the hydroxyl, amino and amido groups in the fibre

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to react more readily with this electrophilic fragment than with the  $\text{SO}_2\text{CH}=\text{CH}_2$  group.

## 2 RESULTS AND DISCUSSION

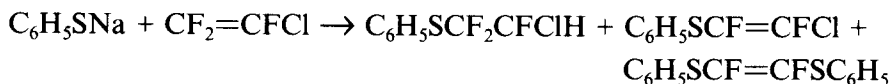
The object of this work was to search for a new reactive fragment for use in fibre reactive dyes. We considered that the difluorovinylsulfone group ( $\text{SO}_2\text{CF}=\text{CFCl}$ ) could be used. Interaction of this with NH or OH groups in fibres could occur both by addition and substitution mechanisms (Scheme 1).



(where R is the residue of the dye; and X is O-cellulose or N-polyamide)

Scheme 1

The synthesis of phenyldifluoroethenylsulfone has been previously described.<sup>1</sup> However, it was obtained only in low yield by a multistage synthesis involving the interaction of chlorotrifluoroethene and sodium thiophenolate. Additionally, the mixture of compounds obtained required separation processes. The pure sulfide thus isolated (containing a chlorinated olefinic link) was then oxidized and dechlorinated, as shown in Scheme 2. It should be noted that the synthesis of compounds containing an  $\text{NH}_2$  group in the phenyl ring by such a synthetic route is not possible.



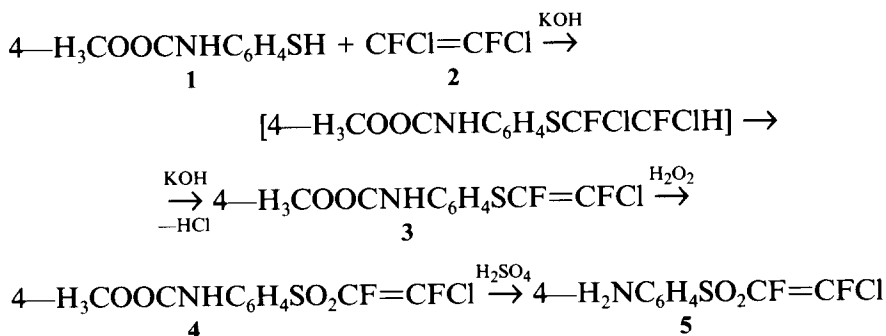
Scheme 2

In the search for more convenient syntheses of arylchlorodifluoroethenylsulfones, we investigated the interaction of 4-N-methoxycarbonylaminothiophenol **1** (a crystalline substance with no unpleasant odour) with 1,2-dichlorodifluoroethene **2**.

Refluxing compound **1** with 1,2-dichlorodifluoroethene **2** in aqueous acetone, in the presence of potassium hydroxide, gave a very facile synthesis of 4-N-methoxycarbonylaminothiophenyl(2-chloro-1,2-difluoroethenyl)sulfide **3**. This reaction presumably occurs in two stages, the first being the addition of 1,2-dichlorodifluoroethene, and the second the

elimination of hydrogen chloride with formation of compound 3. This is evidenced by the fact that substitution products are formed in one stage by the interaction of fluoro-olefins with basic metal thiophenolates only under anhydrous conditions.<sup>2</sup>

The sulfide 3 was oxidized by hydrogen peroxide to give 4-N-methoxycarbonylamino-phenyl(2-chloro-1,2-difluoroethenyl)sulfone 4; the double bond is retained in this reaction. The sulfone 4 was converted with sulphuric acid to 4-aminophenyl(2-chloro-1,2-difluoroethenyl)sulfone 5, as shown in Scheme 3.



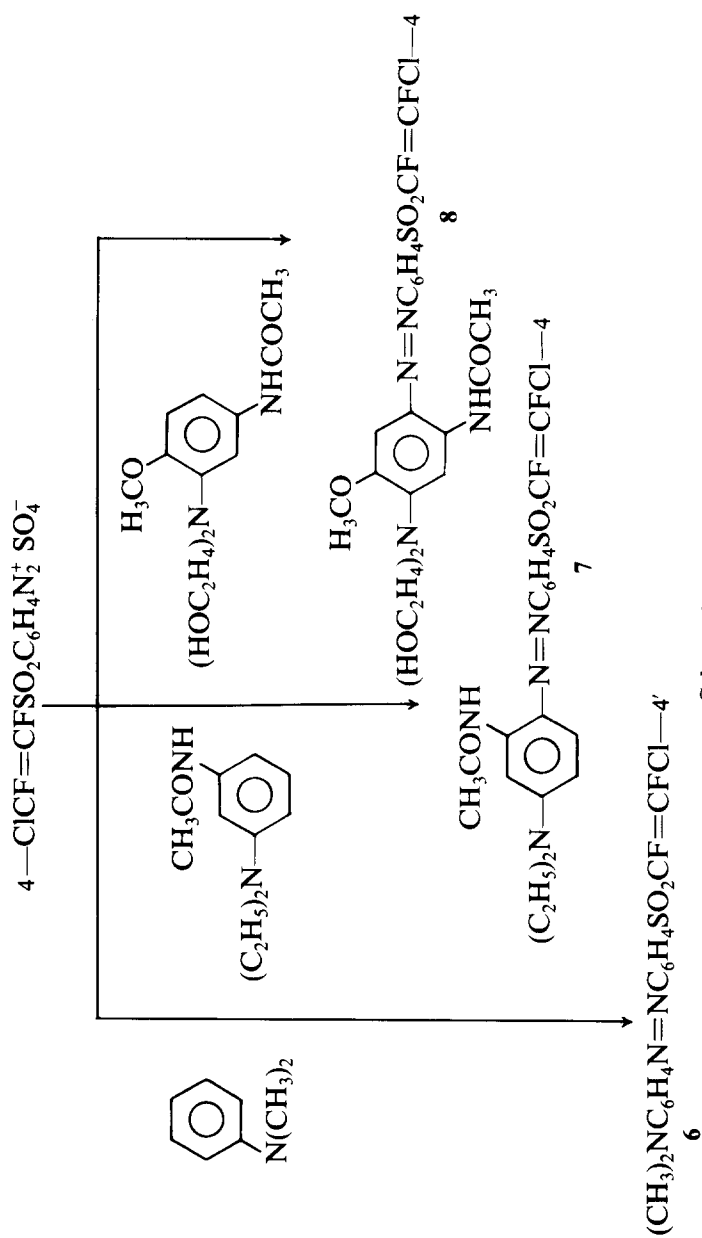
Scheme 3

In accord with <sup>19</sup>F NMR spectroscopy data the sulfide 3 is a mixture of E- and Z-isomers in a 1:2 ratio (see Table 1). Compounds 4 and 5 are mixtures of E- and Z-isomers in a 1:4 ratio. The decrease in the amount of the E-isomer most likely depends on the lower stability of the E-isomer to the action of the oxidizing agent.

Diazotization of the arylamine 5 and coupling with N,N-dimethylaniline, N,N-diethyl-N'-acetyl-2-methoxy-m-phenylenediamine and N,N-bis(2-ethoxyethyl)-N'-acetyl-2-methoxy-m-phenylenediamine gave 4-dimethylamino-4'-[(2-chloro-1,2-difluoroethenyl)sulphonyl]azobenzene 6, 2-acetyl-amino-4-diethylamino-4'-[(2-chloro-1,2-difluoroethenyl)sulphonyl]-azobenzene 7 and 2-acetyl-amino-4-bis(2-ethoxyethyl)amino-5-methoxy-4'-[(2-chloro-1,2-difluoroethenyl)sulphonyl]azobenzene 8, respectively, as presented in Scheme 4. Compounds 6-8 are also mixtures of the E- and Z-isomers in 1:4 ratio (see Table 1). Relevant data for dyes 6-8 are given in Table 2.

Fastness properties of the dyes were evaluated on textured polyamide;<sup>3</sup> results are given in Table 3.

As can be seen from Table 3, for all three dyes the fastnesses to washing and light of polyamide dyed under acid conditions are much lower than values obtained following a two step dyeing process. Further improvement of fastness to wet processes occurs after washing with a surfactant.



Scheme 4

**TABLE 1**  
<sup>19</sup>F NMR Chemical Shifts and Coupling Constants of the Sulfide 3, Sulfones 4, 5 and Dyes 6-8

Dye no.	Z-isomer, - $\delta$ (ppm)		$J_{F^1F^2}$ (Hz)	E-isomer, - $\delta$ (ppm)		$J_{F^1F^2}$ (Hz)
	$F^1$	$F^2$		$F^1$	$F^2$	
3	123.15	105.35	139	112.90	88.90	16.5
4	148.60	98.40	135	138.0	85.20	19
5	147.89	99.78	137	137.77	88.31	10
6	148.21	96.86	136	137.45	83.44	20
7	149.13	96.99	136	137.89	82.73	20
8	150.01	97.04	136	138.32	82.23	20

It may be presumed that under dyeing conditions of pH 4-4.5, chemical interaction of the dyes with polyamide fibre does not occur, and that dyeing occurs under these conditions according to disperse dyeing mechanisms; the fastness to wet treatments of such dyeings is typical for disperse dyes and is not very high. Increase in dyebath pH, however, results in interaction of the dyes with the fibre and formation of a covalent link. The further improvement in fastness which occurs after washing may be explained by the extraction of non-bonded dye.

As evidence for formation of a dye-fibre covalent link under alkaline dyeing conditions, specimens which had been dyed under acid and basic conditions were extracted with boiling ethanol over 5 h. In all cases, samples from alkaline dyeings showed only negligible extraction of dye from the fibre, the extract liquor being only very slightly coloured; the differences in colour of the dyed sample before and after extraction was

**TABLE 2**  
 Yields, Constants and Analysis Data of the Dyes 6-8

Dye no.	Yield (%)	M.p. ( $^{\circ}$ C) (solvent for crystallization)	$\lambda_{max}$ (nm)	Measured values (%)	Brutto formula	Calculated values
6	64	170-171 (benzene)	468	F 9.58 9.76	$C_{16}H_{14}ClF_2N_3O_2S$	F 9.87
7	71	197-198 (benzene)	513	C H 50.84 4.32 51.05 4.43	$C_{20}H_{21}ClF_2N_4O_3S$	C H 51.06 4.47
8	64	163-164 (benzene)	517	C H 47.39 4.30 47.42 4.31	$C_{21}H_{23}ClF_2N_4O_6$	C H 47.36 4.32

**TABLE 3**  
Fastness Properties of Dyes 6-8 on Textured Polyamide-6

Dye no.	Dyeing method <sup>a</sup>	Shade	Fastness properties <sup>b</sup>												Light fastness
			Water				Washing				Perspiration acid				
			1	2	3	4	1	2	3	4	1	2	3	4	
6	1	Yellowish orange	4	3	4	4	4	4-5	4-5	4	4	3-4	3-4	4	5
	2		4	4	5	5	4	4-5	5	5	4	4-5	5	5	5-6
	3		4	5	5	5	4	5	5	5	4	4-5	5	5	6
7	1	Scarlet	4	2-3	3-4	4	4	3-4	4	4	4	2-3	2-3	4	3
	2		4	3-4	4	4	4	4	4-5	4	4	4	3-4	4	5-6
	3		4	4	4	4	4	4-5	4-5	5	4	4	4	4	5-6
8	1	Red	4	2	3-4	4	4	3-4	3-4	4	4	2	4	4	2-3
	2		4	3	4	4	4	3-4	4	4-5	4	3-4	4	4-5	3-4
	3		4	3-4	4	4	4	4-5	5	5	4	3-4	4	4-5	3-4

<sup>a</sup> Dyeing methods: 1. Dyeing at pH 4-4.5, 98°C; 2. acid/alkali technique, i.e. first dyeing at pH 4-4.5, 98°C, then in the same dyebath at pH 10-10.5 without aftertreatment; 3. dyeing as for 2 with aftertreatment of 1 g l<sup>-1</sup> sodium carbonate, 1 g l<sup>-1</sup> scouring surfactant, 60°C.

<sup>b</sup> Fastness properties (ISO methods were used to evaluate the fastness properties): 1. change of dyed fabric shade; 2. staining of polyamide; 3. staining of wool; 4. staining of cotton.

imperceptible. In contrast, the colour of the extract liquor from samples that had been dyed under acid conditions was very intense.

The ratios of the optical densities of the extract liquors were as follows:

$$\text{dye 6, } d^1/d^2 = 5.75$$

$$\text{dye 7, } d^1/d^2 = 3.5$$

$$\text{dye 8, } d^1/d^2 = 3.14$$

where  $d^1$  is the optical density of the solution extracts from examples which were dyed under acid conditions and  $d^2$  is that for specimens that were dyed by the two step process.

These data are in accord with the supposition about the formation of a covalent link between dyes 6-8 and the fibre.

### 3 EXPERIMENTAL

<sup>19</sup>F NMR spectra were recorded on a Bruker WP-200 spectrometer at 188.28 MHz, in deuteroacetone, with CCl<sub>3</sub>F as the external standard. UV spectra were recorded on a Specord UV VIS from solutions in ethanol.

### 3.1 4-N-Methoxycarbonylaminothiophenyl(2-chloro-1,2-difluoroethenyl)sulfide 3

A mixture of 4-N-methoxycarbonylaminothiophenol (5 g), potassium hydroxide (3.2 g), 1,2-dichlorodifluoroethene (7.45 g), acetone (10 ml) and water (5 ml) was refluxed with stirring for 18 h. After cooling the reaction mixture was poured onto ice (200 g); the organic phase was extracted with ether, washed with water, and dried with magnesium sulfate. After removal of solvent, the residue was recrystallized from hexane: yield, 3.4 g (45%); m.p. 59–60°C.

$C_{10}H_8ClF_2NO_2S$  calculated: F 13.06  
measured: F 12.95

### 3.2 4-N-Methoxycarbonylaminothiophenyl(2-chloro-1,2-difluoroethenyl)sulfone 4

A mixture of compound 3 (20 g), glacial acetic acid (46 ml) and hydrogen peroxide (30%, 46 ml) was heated with stirring to 90°C. Stirring was continued for 1 h at 90°C. The reaction mixture was then cooled to 20°C and the resultant solid was filtered and recrystallized from glacial acetic acid: yield, 16.4 g (74%); m.p. 174–175°C.

$C_{10}H_8ClF_2NO_4S$  calculated: F 12.17  
measured: F 12.14

### 3.3 4-Aminophenyl(2-chloro-1,2-difluoroethenyl)sulfone 5

The sulfone 4 (8.1 g) and sulfuric acid (50%, 25 ml) were heated with stirring to 150°C. Stirring was continued at this temperature for 12 h. The reaction mixture was then cooled to 20°C and diluted with water; addition of sodium acetate precipitated the free amine, which was filtered, washed with water, dried and recrystallized from hexane: yield, 6.1 g (92.6%); m.p. 94–95°C.

$C_8H_6ClF_2NO_2S$  calculated: F 15.02  
measured: F 14.93

### 3.4 Preparation of azo dyes 6–8

Aniline 5 (0.01 mol) was dissolved in sulfuric acid (50%, 8 ml). The solution was cooled to below 0°C and a solution of sodium nitrite (0.01 mol) in water (5 ml) was added dropwise with stirring. The diazo liquor was filtered and then added dropwise with stirring to a solution of N,N-dimethylaniline (0.01 mol), N,N-diethyl-N'-acetyl-2-methoxy-m-phenylenediamine or N,N-bis(2-ethoxyethyl)-N'-acetyl-2-methoxy-m-

phenylenediamine (0.01 mol), respectively, in sulfuric acid (10%, 10 ml). After stirring for 30 min, the pH was raised to 6–7 by addition of saturated aqueous sodium acetate. The dyes were filtered, washed with water, dried and recrystallized.

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