Dyes and Pigments 2 (1981) 279–284

AZO DISPERSE DYES WITH POLYFLUOROALKYL GROUPS ATTACHED TO THE NITROGEN ATOM OF THE COUPLING COMPONENT

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SUMMARY

A number of new azo disperse dyes with polyfluoroalkyl groups attached to the nitrogen atom of the coupling component have been prepared The influence of polyfluoroalkyl groups on the colour and properties of azo dyes has been studied The replacement of hydrogen atoms of the methyl group of the coupling component by polyfluoroalkyl radicals causes a hypsochromic shift of absorption maximum in a neutral solution and deepening of the dye colour in an acid solution. All tested dyes showed a high lightfastness on acetate and polyamide fibres

1. INTRODUCTION

Previous publications describe the influence of various fluorine containing substituents in the diazo component on the colour and other characteristics of azo disperse dyes.[1,2] A number of valuable dyes of very good fastness to light, wet treatments and sublimation were found.[3]

Now we report the results on our investigations of the influence of polyfluoroalkyl groups attached to the nitrogen atom of the coupling component on the properties of azo disperse dyes. Dickey was the first to prepare the coupling components of the *N*-fluoroalkyl-*N*-hydroxyalkylaniline type by treating aniline with fluoroalkyl halides followed by hydroxyethylation.[4] His studies of the properties of the azo dyes with such coupling components showed that a decrease in the number of fluorine atoms and their removal from the nitrogen atom led to a bathochromic shift of the absorption band and a reduction in the fastness to light

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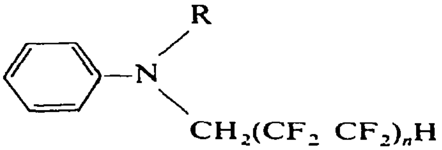
Replacement of two or three atoms of hydrogen at a β-carbon atom by fluorine is optimal for the formation of lightfast dyes.[5,6]

2. RESULTS AND DISCUSSION

We obtained a number of new coupling components A using esters of perfluoroalkylsulphonic acids and telomeric alcohols for the 1,1-dihydropolyfluoroalkylation of arylamines[7] The corresponding azo dyes have also been prepared It was interesting to compare visible absorption maxima of these dyes with the absorption maximum of 4'-nitro-4-dimethylaminoazobenzene (Table 1)



A

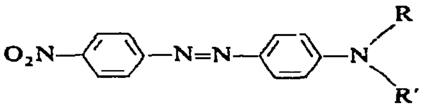
	R	*n*
AI	H	2
AII	CH_3	1
AIII	C_2H_5	1
AIV	C_2H_5	2
AV	C_2H_4CN	1
AVI	C_2H_4OH	1
AVII	C_2H_4OH	2

The replacement of hydrogen atoms of the methyl group in the general formula of the dye of Table 1 by polyfluoroalkyl radicals produces a hypsochromic shift of absorption maxima in neutral solution, and deepening of the colour in acid solution The halochromism index $\Delta\lambda^8$ increased markedly The hypsochromic shift of the absorption maximum in neutral solution is due to the fact that the polyfluoroalkyl groups decrease the electronic density on the nitrogen atom and reduce the electronic transition along the conjugation chain of the dye towards the azo group For the same reason the contribution of the resonance structure with positive charge on the β-nitrogen atom of the azo group grows in acid solution The resonance structures become more equivalent and the colour of the dye deepens markedly in comparison with the dimethylaminoazobenzene derivatives. In acid solution the azo dyes with polyfluoroalkyl groups attached to the nitrogen atom of the coupling component have another absorption band shifted to a shorter wave region (~520 nm) (see Fig. 1) This may correspond to the vibrational transition. Its appearance is probably caused by less pronounced solvent–solute interactions of these dyes

Dyes with coupling component **AIII** and **AVI** give the largest bathochromic shift of absorption maximum (Table 2). When coupling component **AI** is used, the

TABLE 1

VISIBLE ABSORPTION MAXIMA OF 4'-NITRO-4-*N*,*N*-DIALKYLAMINO AZO DYES



R	*R'*	λ_{max} (*nm*)		$\Delta\lambda$
		Ethanol	*Ethanol + HCl*	
CH_3	CH_3	475	508	33
CH_3	$CH_2CF_2CF_2H$	443	544	101
CH_3	$CH_2(CF_2CF_2)_2H$	434	544	110
C_2H_5	$CH_2CF_2CF_2H$	450	546	96
C_2H_5	$CH_2(CF_2CF_2)_2H$	445	546	101
C_2H_4OH	$CH_2CF_2CF_2H$	450	548	98
C_2H_4OH	$CH_2(CF_2CF_2)_2H$	445	550	105

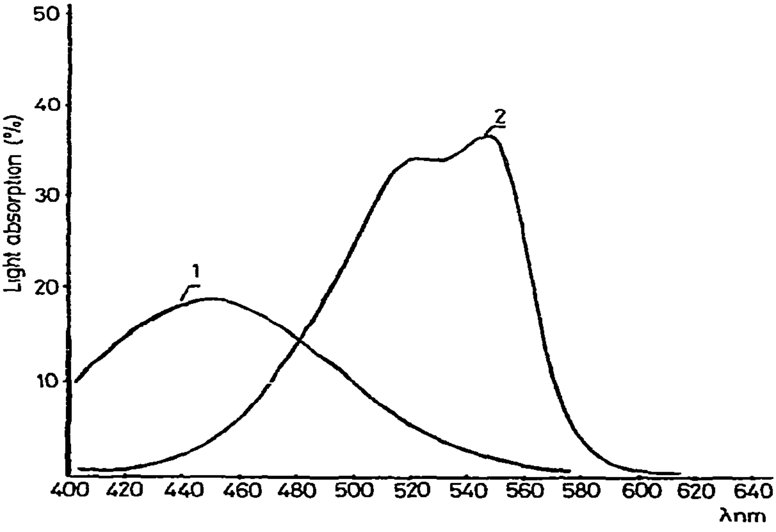
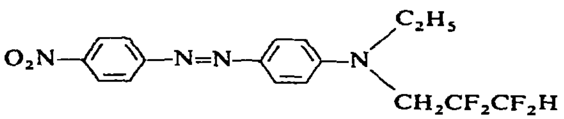


Fig 1 Visible absorption spectra of the dye of formula



(1) in ethanol, (2) in ethanol + HCl

TABLE 2

YIELDS, PHYSICAL PROPERTIES AND LIGHTFASTNESS OF AZO DYES

$B{-}N{=}N{-}A$

B	A																			
	$C_6H_4NHCH_2(CF_2CF_2)_2H$ I				C_2H_5 C_6H_4N $CH_2CF_2CF_2H$ III				C_2H_5 C_6H_4N $CH_2(CF_2CF_2)_2H$ IV				C_2H_4CN C_6H_4N $CH_2CF_2CF_2H$ V				C_2H_4OH C_6H_4N $CH_2CF_2CF_2H$ VI			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3[b]	4
4 $NO_2C_6H_4$				-	134 6 (1)	433	7	48	131 3 (2)	434		60	—	—	—	-	132 (3)	435	5-6Y	70
2 Cl 4 $NO_2C_6H_3$	120 (4)	425	6	33	118 20 (5)	455	7	88	90 2 (6)	448	6	49	138 40 (7)	432	—	19	122 (8)	450	6Y	51
2 Br 4 $NO_2C_6H_3$	45 (9)	384	7	31	-	-			-		—	—	—	—	—	—	118-20 (10)	438	6Y	89
2 Br 4 NO_2 6 Cl C_6H_2	57 (11)	383	7	38	116 18 (12)	402	7	99	94 7 (13)	398	6-7	48	109-11 (14)	388	5	16	142-4 (15)	400	7	81
2 4-di $NO_2C_6H_3$	149 51 (16)	443	5-6	27	122 (17)	470	5 6	49	112 (18)	467	6	29	—	—	—	—	124-6 (19)	470	5-6	65
2 CN 4 $NO_2C_6H_3$	150 (20)	448	7	30	129-30[a] (21)	475	7	60	130 131 (22)	470	6	28	-	—	-	—	141-3 (23)	475	6	54
2 CH_3SO_2 4 $NO_2C_6H_3$	167-9 (24)	440	5 6	22	193[a] (25)	469	6	21	138 9 (26)	463	6 7	27	—	—	—	—	175 (27)	465	6	59
2 6-diCl 4 $NO_2C_6H_2$	52 4 (28)	380	7	34	103-5 (29)	401	7	77	78 80 (30)	399	6 7	34	-	-	—	—	138-40 (31)	402	7	91

Properties 1. Melting points after recrystallization from hexane (dye number in parentheses) 2 λ_{max} (nm) in benzene 3 Lightfastness 4 Yield (%)

[a] From acetone

[b] Y signifies a yellowing of the shade

maximal hypsochromic shift is observed. According to their influence on the bathochromic shift radicals R can be arranged in order:

$$C_2H_5 \geq C_2H_4OH > CH_3 > C_2H_4CN$$

The increase in the number of difluoromethyl groups increases the hypsochromic shift of the absorption maximum of a dye by 6–7 nm. All tested dyes exhibited excellent lightfastness. The highest lightfastness was obtained for dyes with coupling component **AIII**. Table 2 shows that the lightfastness is also greatly dependent on the constitution of the diazo component

Of the tested dyes, 17 exhibited excellent soap fastness (nos. 6, 10, 12, 13, 15, 16, 18, 20–24, 26, 27, 29–31) Dyes nos 15, 24, 25, 27 exhibited the highest fastness to sublimation, and nos. 11, 20 and 28 the lowest (coupling component **AI**)

3 EXPERIMENTAL

The dyes were prepared by condensing the solution of coupling components in acetic acid, acetone or methanol with anilines which diazotized in hydrochloric acid or nitrosylsulphuric acid The crude products were separated by column chromatography and purified by recrystallization

They were then applied to polyester fibre and tested as follows

Polyester fibre (2 ± 0 0002 g) was placed in 140 ml of a solution of the dye specimen in a mixture of 10 ml ethanol and 130 ml water containing 0 14 g 'Nowost' detergent The temperature was raised to 40 °C and the glass dyeing vessel sealed. It was then inserted into the dyeing apparatus and the temperature raised to 130 °C over 35 min followed by a further 30 min at that temperature. The dye bath was then cooled to 40–50 °C, and the dyeing removed and rinsed in warm and cold water successively. It was then reduction cleared using 80 ml of a solution containing 1·95 g sodium hydroxide and 2·0 g sodium dithionite. The temperature was raised to 70 °C over 20 min and maintained at 70 °C for a further 10 min. The dyeing was rinsed in cold water and treated in 80 ml of a 2g litre^{-1} aqueous solution of the detergent 'OP-10' at 80 °C for 30 min, followed by rinsing and air drying Testing was carried out according to the Soviet Union Standard (GOST) 9733-61.[9]

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