Dyes and Pigments 2 (1981) 195–203

SYNTHESIS AND ELECTRONIC SPECTRA OF SOME AZO DISPERSE DYES DERIVED FROM *N*-2,2,2-TRIFLUOROETHYL-1,2,3,4-TETRAHYDROQUINOLINE

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SUMMARY

Several monoazo dyes suitable for transfer printing have been prepared from N-*2,2,2-trifluoroethyl-1,2,3,4-tetrahydroquinoline and compared with their* N-*ethyl counterparts. The presence of a trifluoroethyl group brings about considerable improvements in lightfastness properties on both polyester and nylon. Electron withdrawal by the trifluoroethyl substituent leads to hypsochromic shifts of the visible absorption band and also results in a marked positive halochromism.*

1 INTRODUCTION

Although the presence of terminal bridging in dyes based on 4-aminoazobenzene, such as derivatives of 9-phenylazojulolidine (1)[1] and of 8-phenylazolilolidine (2),[2] leads to notable bathochromic displacements of the visible absorption band together with increased intensities, relative to 4-dialkylaminoazobenzenes, these shifts are accompanied by a significant drop in the lightfastness ratings. Incorporation of a carbonyl group into the julolidine system (3) results in improved lightfastness properties, but the ketojulolidine dyes are not suitable for transfer printing.[3] The presence of a cyanoethyl group (4, Y = CH_2CH_2CN) brings about modest improvements in lightfastness.[4]

Monoazo dyes containing a variety of fluorinated *N*-alkyl groups have been known for some time,[5] such dyes have enhanced lightfastness when at least two fluorine atoms are present on the second or third carbon atom from the nitrogen atom in the *N*-fluoroalkyl substituent. Unfortunately, the syntheses of appropriate fluorinated intermediates are not particularly straightforward, especially when

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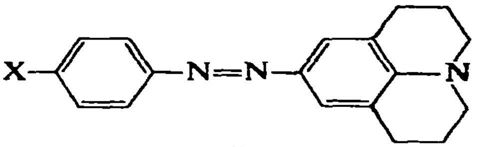
Dyes and Pigments 0143-7208/81/0002-0195/$02.50



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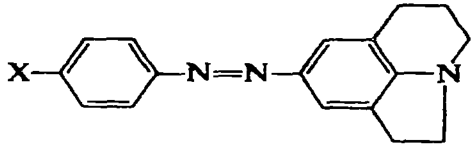

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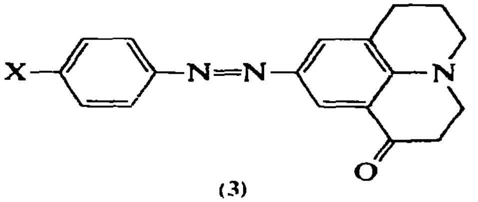

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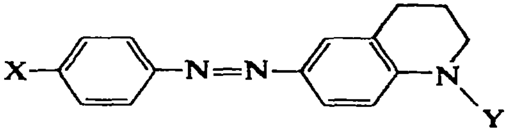


(4)

direct alkylation reactions are involved. However, a new procedure has recently been described for the preparation of *N*-2,2,2-trifluoroethylanilines in which the substituted trifluoroacetylamino group is smoothly reduced using diborane in tetrahydrofuran.[6] It was therefore of interest to apply this method to *N*-trifluoroacetyl-1,2,3,4-tetrahydroquinoline in order to synthesise the novel compound *N*-2,2,2-trifluoroethyl-1,2,3,4-tetrahydroquinoline and examine its use as a dyestuff intermediate.

2 EXPERIMENTAL

2.1 *Dye synthesis*

The dyes were obtained by coupling the appropriate diazonium ion with *N*-ethyl-1,2,3,4-tetrahydroquinoline[7] and *N*-2,2,2-trifluoroethyl-1,2,3,4-tetrahydroquinoline, respectively. The former compound was prepared by quaternisation of 1,2,3,4-tetrahydroquinoline, using ethyl iodide, followed by dealkylation with sodium azide in dimethylformamide.[8] Trifluoroacetylation of 1,2,3,4-tetrahydroquinoline was achieved by using a solution of trifluoroacetic anhydride in carbon tetrachloride[9] and the trifluoroacetyl derivative was reduced by means of diborane in tetrahydrofuran.[6] Conventional methods were used to diazotise the various amines which were then, in most cases, gradually added to a well-stirred dispersion of the coupling component in aqueous acetic acid containing sodium acetate and kept at 0°C, the resulting mixture was basified after 4 h. Owing to a low level of reactivity, successful coupling between the trifluoroethyl derivative and weakly electrophilic diazonium ions only took place in dichloromethane with the aid of sodium dodecylbenzenesulphonate using a phase transfer technique.[10]

The crude dyes were purified by column chromatography on alumina, using a mixture of dichloromethane and cyclohexane as solvent, followed by recrystallisation from ethanol; all the dyes were analytically pure but three products could not be solidified.

2.2. *Spectra*

Absorption spectra were measured with a Unicam SP800 recording spectrophotometer for solutions of the dyes in cyclohexane, ethanol and ethanol containing sufficient hydrogen chloride to obtain optimal protonation of the azo group; details are given in Tables 1 and 2.

2.3 *Dye application*

In each case, a strip of Whatman chromatography paper was immersed for 1 min in a 1 % solution of the dye in dichloromethane or acetone. The excess solution on the surface of the paper was squeezed off between two glass rods and the strip was allowed to dry before being wrapped in a piece of polyester or nylon and then enclosed in metal foil The package was placed between the two plates of a Badische hot press for transfer printing[11] at 200 °C for 30 s

The dyed fabrics were subjected to standard washing fastness and lightfastness tests, the latter involving a Xenon lamp,[12] details are given in Table 3

2 4 N-*Trifluoroacetyl-1,2,3,4-tetrahydroquinoline*

To a stirred solution of 1,2,3,4-tetrahydroquinoline (8 g) in carbon tetrachloride (8 ml) was added a mixture of trifluoroacetic anhydride (12 ml) and carbon tetrachloride (24 ml) during 20 min, after 2 h, the solution was warmed to 40 °C The volatile constituents were removed under reduced pressure, several portions of solvent being added successively to and distilled from the residue before recrystallisation from ethanol The *N*-trifluoroacetyl-1,2,3,4-tetrahydroquinoline (12 4 g, 90 %) was obtained as colourless needles, m.p. 51–52 °C (Found: C, 57 3; H, 4 5; F, 24 8, N, 5 8 %. $C_{11}H_{10}F_3NO$ requires: C, 57 6, H, 4 4, F, 24 9, N, 6 1 %)

2 5 N-2,2,2-*Trifluoroethyl*-1,2,3,4-*tetrahydroquinoline*

A solution of *N*-trifluoroacetyl-1,2,3,4-tetrahydroquinoline (11 45 g) in tetrahydrofuran (50 ml) was added with stirring under nitrogen during 20 min to a 1 M-solution of diborane in tetrahydrofuran (200 ml). After 2 h at room temperature, the reaction mixture was heated under reflux for 21 h The excess of reagent was destroyed by the careful addition of ethanol (5 ml) followed by water (1 ml) to the cold solution Concentrated hydrochloric acid (15 ml) was added to the mixture and tetrahydrofuran (*ca* 180 ml) was removed by distillation The residual solution was poured into water (100 ml) and the mixture was extracted with three portions of dichloromethane (100 ml). The combined extracts were washed with water (25 ml), dried ($MgSO_4$) and the solvent was then evaporated The residue was distilled to yield *N*-2,2,2-trifluoroethyl-1,2,3,4-tetrahydroquinoline (9·2 g, 86 %) as a colourless oil, b.p 108 °C at 6 mmHg (Found. C, 61 4; H, 5 8; F, 26 5, N, 6 3 % $C_{11}H_{12}F_3N$ requires C, 61 4, H, 5·6, F, 26 5, N, 6·5 %)

TABLE 1

MELTING POINTS AND ABSORPTION BANDS OF SOME DYES DERIVED FROM *N*-ETHYL-1,2,3,4-TETRAHYDROQUINOLINE AND *N*-2,2,2-TRIFLUOROETHYL-1,2,3,4-TETRAHYDROQUINOLINE

Dye	*Appearance*	*m p (°C)*	*Cyclohexane*		*Ethanol*		$\Delta\lambda$ *(nm)*
			λ_{max} *(nm)*	$10^{-4}\varepsilon_{max}$	λ_{max} *(nm)*	$10^{-4}\varepsilon_{max}$	
4, X = OMe, Y = Et	Yellow needles	110–111	413	2 96	419	2 83	6
4, X = Me, Y = Et	Orange crystals	88–89	413	2 73	422	2 88	9
4, X = H, Y = Et	Orange liquid		415	2 17	424	2 36	9
4, X = Cl, Y = Et	Orange needles	101–102	422	3 35	439	2 97	17
4, X = Br, Y = Et	Red crystals	95–96	426	2 97	440	3 38	14
4, X = CF_3, Y = Et	Red crystals	97–98	433	2 44	459	3 00	27
4, X = COMe, Y = Et	Red crystals	142–143	443	3 13	475	3 60	32
4, X = CN, Y = Et	Dark red flakes	67–68	450	3 42	479	4 08	29
4, X = NO_2, Y = Et	Brown crystals	103–104	477	3 12	503	3 56	26
5, X = H, Y = Et	Dark red crystals	112–113	448	2 96	476	3 07	28
5, X = NO_2, Y = Et	Dark blue needles	176–177	539	3 47	555	4 60	16
4, X = OMe, Y = CH_2CF_3	Orange liquid		395	2 28	398	2 14	3
4, X = Me, Y = CH_2CF_3	Orange crystals	94–95	394	2 32	398	2 96	4
4, X = H, Y = CH_2CF_3	Orange liquid		396	2 16	398	2 26	2
4, X = Cl, Y = CH_2CF_3	Yellow crystals	103–104	402	3 12	407	2 21	5
4, X = Br, Y = CH_2CF_3	Orange crystals	108–109	403	2 79	409	2 38	6
4, X = CF_3, Y = CH_2CF_3	Red plates	113–114	406	2 34	415	2 27	9
4, X = COMe, Y = CH_2CF_3	Orange crystals	141–142	416	2 11	428	2 55	12
4, X = CN, Y = CH_2CF_3	Orange crystals	118–119	420	3 16	431	2 82	11
4, X = NO_2, Y = CH_2CF_3	Red flakes	123–124	435	2 71	450	2 59	15
5, X = H, Y = CH_2CF_3	Orange needles	128–129	420	3 06	431	2 38	11
5, X = NO_2, Y = CH_2CF_3	Purple needles	160–161	471	3 14	499	3 43	28

3. RESULTS AND DISCUSSION

3.1. *Visible spectra*

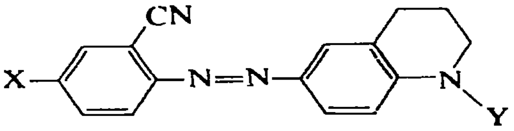
The spectral characteristics of the two groups of dyes are shown in Tables 1 and 2 Bathochromic shifts of the visible absorption band are observed on increasing the solvent polarity (Table 1) as expected for a system in which the excited state is more polar than the ground state [13] This positive solvatochromism is generally less pronounced for the trifluoroethyl dyes since electron withdrawal by the CH_2CF_3 group will influence the transfer of electron density from the terminal nitrogen atom (6). The polarity of the excited state, represented approximately by (7), will consequently be diminished

TABLE 2
HALOCHROMISM OF SOME AZO DYES IN ETHANOLIC HYDROGEN CHLORIDE

Dye	*EtOH*			*EtOH + HCl*		
	λ_{max} (*nm*)	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$ (*nm*)	λ_{max} (*nm*)	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$ (*nm*)
4, X = OMe, Y = Et	419	2 83	-5^a	564	5 95	145
4, X = Me, Y = Et	422	2 88	-2^a	534	6 17	112
4, X = H, Y = Et	424	2 36		523	5 50	99
4, X = Cl, Y = Et	439	2 97	15^a	526	6 01	87
4, X = Br, Y = Et	440	3 38	16^a	527	6 78	87
4, X = CF_3 Y = Et	459	3 00	35^a	506	6 10	47
4, X = COMe, Y = Et	475	3 60	51^a	525	7 01	50
4, X = CN, Y = Et	479	4 08	55^a	515	7 55	36
4, X = NO_2, Y = Et	503	3 56	79^a	517	7 20	14
5, X = H, Y = Et	476	3 07	52^a	507	4 65	31
5, X = NO_2, Y = Et	555	4 60	131^a	501	5 93	−54
4, X = OMe, Y = CH_2CF_3	398	2 14	0^b	568	5 84	170
4, X = Me, Y = CH_2CF_3	398	2 96	0^b	554	6 30	156
4, X = H, Y = CH_2CF_3	398	2 26		545	4 81	147
4, X = Cl, Y = CH_2CF_3	407	2 21	9^b	550	6 60	143
4, X = Br, Y = CH_2CF_3	409	2 38	11^b	551	6 70	142
4, X = CF_3, Y = CH_2CF_3	415	2 27	17^b	538	6 26	123
4, X = COMe, Y = CH_2CF_3	428	2 55	30^b	553	6 33	125
4, X = CN, Y = CH_2CF_3	431	2 82	33^b	546	6 85	115
4, X = NO_2, Y = CH_2CF_3	450	2 59	52^b	546	6 87	96
5, X = H, Y = CH_2CF_3	431	2 38	33^b	516	4 38	85
5, X = NO_2, Y = CH_2CF_3	499	3 43	101^b	511	5 66	12

[a] Relative to (4, X = H Y = Et)
[b] Relative to (4, X = H, Y = CH_2CF_3)

Replacement of the *N*-ethyl group in (4; Y = C_2H_5) by the 2,2,2-trifluoroethyl substituent brings about a significant hypsochromic shift of the first band (Table 2), varying from 26 nm for the parent dye (4; X = H) to 53 nm for the *p*-nitro derivative (4; X = NO_2), together with a small but consistent decrease in absorption intensity. Strong inductive electron withdrawal by the CH_2CF_3 group leads to a reduction in the electron releasing tendency of the terminal nitrogen atom and a consequent hypsochromic movement of the visible absorption band since the position of λ_{max} is related to the basicity of the molecule.[13] The hypsochromic influence of the trifluoroethyl group more than compensates for the bathochromic effect of the terminal bridge so that the λ_{max} values of these dyes are at somewhat shorter wavelengths than those of corresponding compounds derived from diethylaminoazobenzene.[14]



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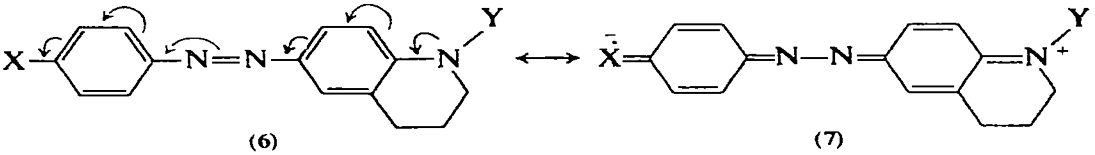
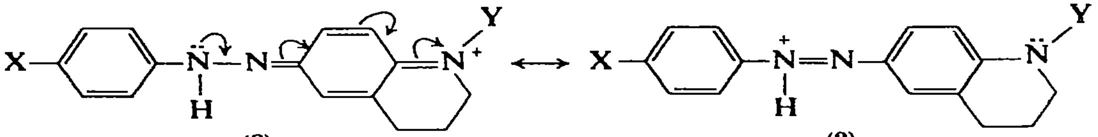


(6) (7)

For both series of dyes, the wavelength shift produced by an acceptor substituent (X) is approximately related to the appropriate Hammett σ-constant. This finding can be accounted for qualitatively in terms of the valence-bond resonance approach by regarding the dye as a resonance hybrid of two extreme canonical structures, (6) and (7), of different energies.[13] Factors which tend to bring the two structures closer in energy lead to bathochromic shifts of the first band. Thus, the high-energy dipolar structure (7) is stabilised when X is an electron withdrawing substituent. A similar explanation obtains by taking structure (6) to be a fairly close approximation to the ground state of the molecule and structure (7) as a reasonable approximation to the excited state.

The 2-cyano-4-nitro derivative (5, $X = NO_2$, $Y = C_2H_5$) demonstates exact additivity of substituent effects (Table 2) in accordance with the absence of steric hindrance.[15] In the case of the trifluoroethyl analogue (5; $X = NO_2$, $Y = CH_2CF_3$), however, the additivity is only approximate.

It is well known that in aminoazobenzene dyes the first band generally moves to longer wavelengths in acid solution (halochromism) owing to formation of the resonance-stabilised azonium ion, (8)↔(9), by protonation at the azo group; the tautomeric ammonium ion absorbs in the ultraviolet.[13] Although the azonium ion can be regarded as a charge-resonance system, it is best represented in the ground state by the quinonoid structure (8) so that the visible absorption band is associated with a migration of electron density from the β-nitrogen atom. Thus, the direction of charge migration accompanying electronic excitation is the opposite to that associated with the neutral dyes. Consequently, the usual positive halochromism observed on protonation increases as the electron donating strength of substituent X increases; conversely, the bathochromic shift diminishes when X is electron withdrawing Qualitatively, if structure (9) predominates in the excited state then electron donors will stabilise this whereas electron acceptors will stabilise the ground state structure (8) and *vice versa* Displacement of the absorption band is again approximately proportional to the Hammett σ value of the substituent for both series of dyes (4) (Table 2). It is interesting that the azonium species for the trifluoroethyl dyes (8; $Y = CH_2CF_3$) absorb at somewhat longer wavelengths than their *N*-ethyl analogues (8, $Y = C_2H_5$) in contrast to the behaviour of the neutral dyes This bathochromic movement can be associated with inductive electron withdrawal by the CH_2CF_3 group which effectively reduces the energy required for the molecule to attain the excited state Electron withdrawal by the trifluoroethyl group results in a decrease in the basicity of the system as a whole so that considerably more acid is required to protonate these dyes than the corresponding *N*-ethyl compounds.



(8) (9)

Owing to the opposite directions of charge migration accompanying electronic excitation in the neutral dyes and their azonium cations, the long-wavelength bands of the two species converge with increasing electron accepting strength of X Excellent linear correlations are found between the wavelength shift ($\lambda_{azonium} - \lambda_{neutral}$), or more strictly the frequency difference, and the appropriate σ-constants, in accordance with theoretical expectations [16] The value of $\Delta\lambda$ decreases steadily as the electron withdrawing capacity of X increases (Table 2), the absolute values being smaller in the case of the *N*-ethyl series. If the overall electron withdrawal is sufficiently large, the bands may in fact cross so that the azonium ion absorbs at a shorter wavelength than the neutral molecule.[3] Thus, the 2-cyano-4-nitro dye (5, $X = NO_2$, $Y = C_2H_5$) exhibits a significant negative halochromism (54 nm). The analogous trifluoroethyl derivative (5; $X = NO_2$, $Y = CH_2CF_3$) shows a small positive halochromism (12 nm) because the electron withdrawing effect of the CH_2CF_3 substituent tends to counterbalance that of the cyano and nitro groups

3.2. *Dye characteristics*

Owing to the hypsochromic influence of the CH_2CF_3 group, the trifluoroethyl dyes (4; $Y = CH_2CF_3$) have rather different colours from their ethyl analogues (4; $Y = C_2H_5$). Thus, for example, the 2-cyano-4-nitro derivative (5; $X = NO_2$, $Y = CH_2CF_3$) is red whereas the relevant *N*-ethyl compound (5, $X = NO_2$, $Y = C_2H_5$) is purple.

Both series of azo dyes are suitable for transfer printing and have satisfactory fastness to washing on polyester and moderate fastness on nylon.[17] The *N*-ethyl derivatives (4; $Y = C_2H_5$) have better lightfastness ratings than their julolidine counterparts (1).[3] By comparison with the *N*-ethyl dyes, the trifluoroethyl derivatives show considerable improvements in lightfastness properties on both polyester and nylon (Table 3). The lightfastness is dependent on the substituents attached to the terminal nitrogen atom and is generally improved by electron withdrawing groups.[18] The lightfastness ratings of the trifluoroethyl dyes on polyester tend to increase with the electron withdrawing capacity of the substituents in the diazo component, in accordance with earlier findings [13] The same trend is observed on nylon, in contrast to the results of Muller [19] More recent work by Sunthankar and Thanumoorthy,[20] which partly duplicates that of Muller, reveals no clear relationship between photostability on nylon and the electronic effects of substituents in the acceptor ring

TABLE 3
LIGHTFASTNESS RATINGS OF SOME AZO DYES ON NYLON AND POLYESTER

Substituents	N-*Ethyl dyes* (4 $Y = Et$)		N-*Trifluoroethyl dyes* (4, $Y = CH_2CF_3$)	
	Nylon	*Polyester*	*Nylon*	*Polyester*
4-CH_3	2	3	2	4
4-Cl	2	3	2	4
4-Br	2	3	2	4–5
4-CF_3	2–3	2	5	4
4-$COCH_3$	2–3	3	4	5
4-CN	3	3	6	6
4-NO_2	3	3	6	6–7
2-CN	3	3	6	5
2-CN,4-NO_2	3	3	6–7	7

It is generally assumed, largely on the basis of indirect evidence gained from comparative studies of fading rates, that the irreversible fading in light of azo dyes is associated with oxidative cleavage of the azo linkage [21] Griffiths[22] suggests, however, by analogy with the susceptibility of many simple amino compounds towards photo-oxidation, that the oxidative degradation of an aminoazo dye occurs at the amino group rather than at the azo linkage On the basis of the present results, it is not possible to conclude whether photochemical attack takes place at the terminal nitrogen atom or at the azo group Nevertheless, it is clear that improved conjugation by the terminal nitrogen lone pair electrons leads to a build up of electron density at the azo group and a decrease in lightfastness This build up is countered by the presence of electron attracting substituents in the diazo component or at the terminal nitrogen atom It also remains an open question as to whether photochemical degradation on nylon proceeds by a photo-oxidative or a photoreductive mechanism, although it can be argued that the data given in Table 3 tend to support the former process

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