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Synthesis and Electronic Spectra of some Azo Disperse Dyes derived from *N*-Alkyl-1,2,3,4-tetrahydroquinoline

G. Hallas & K. Y. Zhai

Department of Colour Chemistry, The University, Leeds LS2 9JT, UK

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ABSTRACT

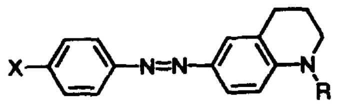
Three series of dyes derived from N-*alkyl-1,2,3,4-tetrahydroquinoline (1; R = propyl, butyl and isobutyl) have been examined. The spectroscopic properties of identically substituted dyes in each series are very similar. Moderate light-fastness ratings were observed for all the dyes but sublimation fastness improved with increase in size of the alkyl group. Copyright © 1996 Elsevier Science Ltd*

Keywords: Monoazo dyes, *N*-alkyl-1,2,3,4-tetrahyroquinoline, synthesis, absorption spectra.

INTRODUCTION

It is well established that the presence of terminal bridging in dyes based on 4-aminoazobenzene, such as derivatives of 9-phenylazojulolidine[1] and of 8-phenylazolilodine,[2] leads to notable bathochromic displacements of the visible absorption band together with increased intensities, relative to 4-dialkylaminoazobenzenes. However, these changes are accompanied by a significant drop in light-fastness ratings; the latter can be improved by incorporating a carbonyl group into the julolidine system.[3] Similar but less pronounced changes are observed in monoazo dyes derived from *N*-substituted-1,2,3,4-tetrahydroquinoline (**1**).

A series of dyes derived from *N*-methyl-1,2,3,4-tetrahydroquinoline (kairoline) (**1**; R = CH_3) was found to give moderately good light-fastnesss ratings (4–5) on both nylon and polyester.[4] Related dyes based on *N*-methylindoline (**2**), in which the six-membered terminal ring system has been replaced by a five-membered heterocycle, show some deterioration in



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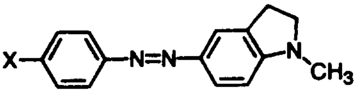
light-fastness properties on synthetic-polymer fibres.[5] The presence of a five-membered ring leads to diminished π-interaction and to consequent hypsochromic and hypochromic shifts of the visible absorption band, relative to the corresponding dyes derived from kairoline. When the methyl group of the kairoline component is replaced by ethyl (**1**; $R = C_2H_5$), a decrease in the light-fastness ratings is observed on both nylon and polyester.[6] The presence of a cyanoethyl group (**1**; $R = CH_2CH_2CN$) brings about only modest improvements in light fastness,[4] whereas the incorporation of a 2,2,2-trifluoroethyl group (**1**; $R = CH_2CF_3$) results in considerable improvements in light-fastness properties.[6] The properties of dyes containing a cyanomethyl group (**1**; $R = CH_2CN$) will be reported in a later publication. The unexpected difference in light-fastness ratings between the kairoline dyes (**1**;

TABLE 1
Absorption Bands of some Dyes derived from *N*-Alkyl-1,2,3,4-tetrahydroquinolines

Dye **1**	Cyclohexane		Ethanol		
	λ_{max} (nm)	$10^{-4}\ \varepsilon_{max}$	λ_{max} (nm)	$10^{-4}\ \varepsilon_{max}$	$\Delta\lambda$ (nm)
X = OMe, R = Pr	415	3.35	420	2.84	5
X = Me, R = Pr	415	3.30	423	2.89	8
X = H, R = Pr	416	3.16	425	2.71	9
X = Br, R = Pr	427	3.65	446	2.13	19
$X = CF_3$, R = Pr	435	3.39	454	3.09	19
X = COMe, R = Pr	445	4.13	476	3.46	31
X = CN, R = Pr	452	3.70	479	3.62	27
$X = NO_2$, R = Pr	475	3.30	502	3.33	27
X = OMe, R = Bu	415	3.33	422	2.78	7
X = Me, R = Bu	415	3.24	423	2.83	8
X = H, R = Bu	417	3.11	426	2.59	9
X = Br, R = Bu	428	3.57	448	3.01	20
$X = CF_3$, R = Bu	435	3.41	456	3.06	21
X = COMe, R = Bu	446	3.63	478	3.49	32
X = CN, R = Bu	453	3.71	481	3.62	28
$X = NO_2$, R = Bu	477	4.00	505	3.58	28
X = OMe, $R = Bu^i$	415	3.30	422	2.86	7
X = Me, $R = Bu^i$	415	3.28	423	2.91	8
X = H, $R = Bu^i$	416	3.17	425	2.71	9
X = Br, $R = Bu^i$	428	3.49	446	2.90	18
$X = CF_3$, $R = Bu^i$	435	3.38	455	3.02	20
X = COMe, $R = Bu^i$	446	3.57	477	3.42	31
X = CN, $R = Bu^i$	452	3.67	480	3.65	28
$X = NO_2$, $R = Bu^i$	475	3.63	504	3.44	29

$R = CH_3$) and their *N*-ethyl counterparts (**1**; $R = C_2H_5$) made it of interest to examine the effects of larger alkyl groups.



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RESULTS AND DISCUSSION

Visible spectra

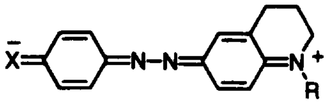
The spectral characteristics of three groups of dyes (**1**; $R = CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$ and $CH_2CH(CH_3)_2$, respectively) are shown in Table 1 and Table 2. Bathochromic shifts of the visible absorption band are observed on increasing the solvent polarity (Table 1), as expected for a system in

TABLE 2
Halochromism of some Dyes derived from *N*-Alkyl-1,2,3,4-tetrahydroquinolines

Dye 1	Ethanol		Ethanol + HCl		
	λ_{max} (nm)	10^{-4} ε_{max}	λ_{max} (nm)	10^{-4} ε_{max}	$\lambda_{azonium} - \lambda_{neutral}$
X = OMe, R = Pr	420	2.84	566	6.08	146
X = Me, R = Pr	423	2.89	537	6.01	114
X = H, R = Pr	425	2.71	525	5.85	100
X = Br, R = Pr	446	2.13	529	6.30	83
X = CF_3, R = Pr	454	3.09	512	6.08	58
X = COMe, R = Pr	476	3.46	525	6.59	49
X = CN, R = Pr	479	3.62	515	6.42	36
X = NO_2, R = Pr	502	3.33	519	6.86	17
X = OMe, R = Bu	422	2.78	564	6.06	142
X = Me, R = Bu	423	2.83	537	5.89	114
X = H, R = Bu	426	2.59	525	5.75	99
X = Br, R = Bu	448	3.01	529	6.32	81
X = CF_3, R = Bu	456	3.06	512	6.16	56
X = COMe, R = Bu	478	3.49	525	6.59	47
X = CN, R = Bu	481	3.62	516	5.62	35
X = NO_2, R = Bu	505	3.58	519	7.10	14
X = OMe, R = Bu^i	422	2.86	570	5.99	148
X = Me, R = Bu^i	423	2.91	539	6.15	116
X = H, R = Bu^i	425	2.71	526	5.92	101
X = Br, R = Bu^i	446	2.90	531	6.00	85
X = CF_3, R = Bu^i	455	3.02	514	6.16	59
X = COMe, R = Bu^i	477	3.42	526	6.62	49
X = CN, R = Bu^i	480	3.65	518	6.54	38
X = NO_2, R = Bu^i	504	3.44	521	6.95	17

which the excited state is more polar than the ground state.[7] This positive solvatochromism is very similar for each series of dyes and close to that observed for the corresponding ethyl derivatives (**1**; $R = C_2H_5$).[6]

For each series of dyes, the wavelength shift produced by an acceptor substituent (X) is approximately related to the appropriate Hammett σ-constant, in accordance with the valence-bond resonance approach.[7] Thus, the high-energy dipolar excited state (**3**) is stabilised when X is an electron-withdrawing substituent.



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The usual positive halochromism shown by dyes of this type (Table 2) increases as the electron-donating strength of substituent X increases, the displacement again being approximately proportional to the Hammett σ-value of the substituent. Owing to the opposite directions of charge migration accompanying electronic excitation in the neutral dyes and their azonium cations, **4** ↔ **5**, the long-wavelength bands of the two species (Scheme 1) converge with increasing electron-accepting strength of X. Excellent linear correlations are found between the wavelength shift, $\lambda_{azonium} - \lambda_{neutral}$, and the appropriate σ-constants, in accordance with theoretical expectations.[8] The value of $\Delta\lambda$ decreases steadily, in a similar manner for each series, as the electron-withdrawing capacity of X increases (Table 2).

Dye characteristics

All the azo dyes were applied to polyester fabric in a high-temperature dyeing machine. After reduction clearing, the light-fastness ratings of the dyed samples were determined. For each series, the measured values (3) were very close to those observed previously for the *N*-ethyl derivatives (**1**; $R = C_2H_5$),[6] being insensitive to substituent effects in the acceptor ring. It is not clear why the kairoline dyes (**1**; $R = CH_3$)[4] appear to possess superior light-fastness properties.

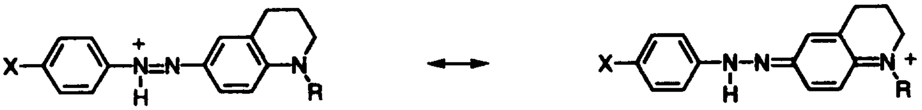

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TABLE 3

Yields, Boiling Points and Appearance of some Derivatives of 1,2,3,4-Tetrahydroquinoline

Derivative	Yield (%)	Boiling Point (°C)	Appearance
N-*N*-Propionyl	77	52*	Pale yellow solid
N-Propyl	81	110–111 at 3.0 mmHg	Colourless oil
N-Butyryl	78	147–149 at 2.8 mmHg	Colourless oil
N-Butyl	76	119–120 at 2.8 mmHg	Colourless oil
N-Isobutyryl	86	43*	Colourless solid
N-Isobutyl	79	110–111 at 2.7 mmHg	Colourless oil

*Melting point.

TABLE 4

Yields, Purification Methods, Melting Points and Appearance of some Dyes derived from *N*-Alkyl-1,2,3,4-tetrahydroquinolines

Dye **1**	Purification method	Yield (%)	Melting point (°C)	Appearance
X = OMe, R = Pr	A	23	78.2	Yellow crystals
X = Me, R = Pr	A	32	81.6	Orange crystals
X = H, R = Pr	B	8	64.4	Orange crystals
X = Br, R = Pr	B	6	64.0	Red crystals
X = CF_3, R = Pr	A	38	90.4	Red rods
X = COMe, R = Pr	C	19	86.5	Red crystals
X = CN, R = Pr	B	13	91.5	Red flakes
X = NO_2, R = Pr	B	13	78.6	Maroon crystals
X = OMe, R = Bu	A	16	80.0	Orange–yellow crystals
X = Me, R = Bu	B	19	73.0	Reddish-orange powder
X = H, R = Bu	A	26	53.4	Orange crystals
X = Br, R = Bu	B	11	88.2	Orange–red crystals
X = CF_3, R = Bu	A	23	62.2	Maroon powder
X = COMe, R = Bu	C	10	69.0	Red microcrystals
X = CN, R = Bu	B	13	92.0	Red needles
X = NO_2, R = Bu	B	18	85.3	Red–brown needles
X = OMe, R = Bu^i	A	28	63.0	Yellow rods
X = Me, R = Bu^i	A	24	68.0	Dark yellow crystals
X = H, R = Bu^i	B	32	73.0	Orange–yellow powder
X = Br, R = Bu^i	B	9	60.9	Orange–red crystals
X = CF_3, R = Bu^i	A	23	62.2	Orange–red flakes
X = COMe, R = Bu^i	B	19	95.6	Red needles
X = CN, R = Bu^i	B	10	102.1	Red flakes
X = NO_2, R = Bu^i	B	21	89.5	Red crystals

A, Silica column in toluene; crystallise from light petroleum (b.p. 40–60°C).

B, Alumina column in toluene; crystallise from light petroleum (b.p. 40–60°C).

C, Alumina column in 1:1 methylene chloride:toluene; silica column in toluene; crystallise from light petroleum (b.p. 40–60°C).

The sublimation behaviour of the various dyes was examined by transfer printing on to polyester film, followed by spectroscopic assessment. It was not possible to distinguish between the *N*-butyl and *N*-isobutyl isomers, but both series are more difficult to sublime than their *N*-propyl counterparts, in accordance with variations in relative molecular mass and in molecular volume.

EXPERIMENTAL

Attempts to prepare the *N*-substituted-1,2,3,4-tetrahydroquinolines by quaternisation and dealkylation[9] or by a one-pot reduction–alkylation procedure,[10] using the appropriate carboxylic acid and $NaBH_4$, resulted in relatively low yields. Good yields of the required amines were achieved by a two-step synthesis involving acylation followed by reduction[11] of the resulting amides with $LiAlH_4$. Details are given in Table 3; all the compounds had satisfactory microanalytical data. Conventional methods were used to diazotise the various amines.[3]

Coupling reactions were carried out at pH 4–5 and 0–5°C in a mixture of acetic acid and sodium acetate. After 2 h at room temperature, the crude material was purified by column chromatography on alumina or silica followed by recrystallisation; details are given in Table 4. In each case, satisfactory microanalytical data were obtained and dye purity was confirmed by differential scanning calorimetry.

REFERENCES

1. Castelino, R. W. & Hallas, G., *J. Chem. Soc. (B)* (1971) 793.
2. Hallas, G., Ho, W. L. & Todd, R., *J. Soc. Dyers Colour.*, **90** (1974) 121.
3. Hallas, G. & Ng, K. L., *J. Soc. Dyers Colour.*, **93** (1977) 284.
4. Hallas, G. & Saadatjou, N., *J. Soc. Dyers Colour.*, **97** (1981) 282.
5. Hallas, G. & Ho, S. F., *J. Soc. Dyers Colour.*, **98** (1982) 429.
6. Aliwarga, H. & Hallas, G., *Dyes and Pigments*, **2** (1981) 195.
7. Hallas, G., *J. Soc. Dyers Colour.*, **95** (1979) 285.
8. Griffiths, J., *J. Soc. Dyers Colour.*, **88** (1972) 106.
9. Ho, T.-L., *Synth. Commun.*, **3** (1973) 99.
10. Gribble, G. W. & Heald, P. W., *Synthesis*, **10** (1975) 650.
11. Hallas, G. & Taylor, D. C., *J. Chem. Soc.* (1964) 1518.