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Colour and halochromic properties of azo dyes derived from 10-methyl-9-methylene-9,10-dihydroacridine as coupling component

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Dedicated to Dr. Arnold Peters on his retirement, in appreciation of our many years of friendship and his invaluable contributions to the field of dye chemistry

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Abstract

10-Methyl-9-methylene-9,10-dihydroacridine, in the form of its methylsulfate salt, couples to arenediazonium ions to give highly bathochromic azo dyes. These are typical donor–acceptor chromophoric systems, exhibiting a progressive bathochromic shift as the electron withdrawing strength of the diazonium component increases. Thus λ_{max} values range in ethanol from 561 nm for the 4-*N,N*-dimethylaminophenylazo derivative to 650 nm for the 2-cyano-4-nitrophenylazo dye. Further increases in the electron withdrawing effect of the arylazo substituent lead to a hypsochromic shift, as evidenced by the 3,5-dinitro-2-thienylazo derivative, with a λ_{max} value of 610 nm in ethanol. The arylazo derivatives are strongly basic, with pK_b values in the range 4.6–8.2, and show negative halochromism. Thus protonation gives azonium cations which absorb at shorter wavelengths than the parent dyes, and in some cases the pH-induced visual colour change is sufficiently pronounced to render the dyes of value as indicators. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Acridine azo dyes; Halochromism; p*K* properties; pH Indicators

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1. Introduction

It is known that donor–acceptor and cyanine-type dye chromophores derived from 10-methyl-9-methylene-9,10-dihydroacridine **1** show exceptional bathochromic properties. For example, the cationic dye **2** absorbs at ca. 800 nm in dichloromethane, even though the longitudinal conjugation pathway between the terminal nitrogen atoms extends over only 9 atoms [1]. Similarly the dye **3** absorbs at 822 nm in dichloromethane, even though it is only a trimethine cyanine [2].

This exceptional bathochromic effect may be attributed to the powerful electron releasing effect of the dihydroacridine residue of **1** and/or the powerful electron accepting effect of the corresponding acridinium ion. The high nucleophilicity of the enamine **1** enables it to couple with diazonium ions to give azo dyes **4**, but little is known about their chromophoric properties. We now describe details of the synthesis and visible absorption spectra of representative examples of dihydroacridine azo

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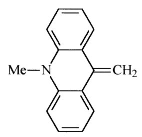
dyes **4,** and also report their exceptional halochromic properties.



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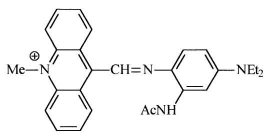

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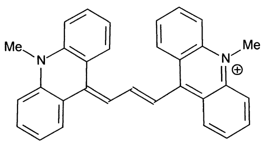

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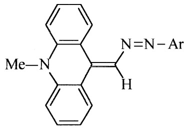

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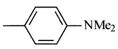

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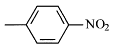

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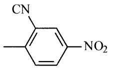

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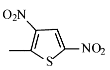


2. Experimental

2.1. N-*methylacridine*

Diphenylamine (13 g, 0.08 mol) and zinc chloride (40 g, 0.3 mol) were stirred in acetic acid (10 ml) at 220°C for 8 h. The residue was digested in 10% sulfuric acid and the solution made strongly alkaline with concentrated ammonia solution The resulting precipitate was dissolved in toluene and extracted into 10% sulfuric acid. The acidic phase was neutralised with aqueous ammonia giving a yellow precipitate of *N*-methylacridine, which was filtered off and dried in an oven (11.26 g, 76%), m.p. 117–118°C (lit.[1] 117–118°C).

2.2. *9,10-Dimethylacridinium methylsulfate* **5**

N-Methylacridine (1.5 g, 0.007 mol) and dimethyl sulfate (1.5 g, 0.01 mol) were stirred under reflux in toluene (30 ml) for 6 h. After cooling the solution, the precipitate was collected, washed with toluene and dried in an oven, giving 9,10-dimethylacridinium methylsulfate as a bright yellow powder (1.03 g, 71%), m.p. 235°C decomp. (lit. [3] 233°C decomp.).

2.3. *4-*N,N-*Dimethylaminobenzenediazonium tetra-fluoroborate*

4-*N,N*-Dimethylaminoaniline sulfate (4.68 g, 0.02 mol) was dissolved in tetrafluoroboric acid (40%, 20 ml). Water (40 ml) was added to the acidic solution and the reaction cooled using an ice bath. When the temperature had dropped below 5°C, a solution of sodium nitrite (1.38 g, 0.02 mol) in water (20 ml) was added dropwise over fifteen minutes. The mixture was stirred for twenty minutes and the yellow solid filtered off and dried in a dessicator. The product was recrystallised from toluene containing 10% ethanol to give yellow crystals of the tetrafluoroborate salt (85%).

2.4. *4-Nitrobenzenediazonium tetrafluoroborate*

4-Nitroaniline (21 g, 0.11 mol) was dissolved in boiling concentrated hydrochloric acid (15 ml) and the clear solution was cooled rapidly with an ice bath. A solution of sodium nitrite in ice water (20 g) was added rapidly, and the reaction was stirred for 30 min. Sodium tetrafluoroborate (16.4 g, 0.15 mol) dissolved in water (50 ml) was added to the diazonium solution, and stirring continued for one hour. The yellow solid was filtered off and dried in a dessicator (27.5 g, 54.7%).

2.5. *4-*N,N-*Dimethylaminophenylazo dye* **4a**

9,10-Dimethylacridinium methylsulfate (0.32 g, 0.001 mol) and 4-*N,N*-dimethylamino-benzenediazonium tetrafluoroborate (0.23 g, 0.001 mol) were stirred in water (10 ml) for 1 h. The resultant burgundy solid was filtered off, washed with copious amounts of water, and then dried in an oven. The solid was chromatographed over alumina, using toluene as eluent, giving (**4a**) as deep red crystals (0.08 g, 24%). Mass spectrum: found $m/z = 354$. $C_{23}H_{22}N_4$ requires $M = 354$.

2.6. *4-Nitrophenylazo dye* **4b**

9,10-Dimethylacridinium methylsulfate (0.96 g, 0.003 mol) and p-nitrobenzenediazonium tetrafluoroborate (0.69 g, 0.003 mol) were stirred in water (20 ml) for 1 h. The resultant blue solid was filtered off, washed with copious amounts of water and dried in an oven. The solid was chromatographed over alumina, using toluene as eluent, giving the dye (**4b**) as blue crystals (0.55 g, 51%). Found: C, 70.15; H 4.04; N, 15.2% ; M^+ 356. $C_{21}H_{16}N_4O_2$ requires C,70.78; H,4.53; N,15.72% ; M 356.

2.7. *2-Cyano-4-nitrophenylazo dye* **4c**

2-Cyano-4-nitroaniline (0.16 g, 0.001 mol) was dissolved in concentrated sulfuric acid (5 ml) cooled in an ice bath. When the temperature had fallen below 5°C, nitrosyl sulfuric acid (40%) (0.3 g) was added and stirring continued for 2 h below 10°C. The diazonium solution was slowly added to 9,10-dimethylacridinium methylsulfate (0.32 g, 0.001 mol) in water (40 ml), whilst using dilute sodium hydroxide to ensure that the solution was slightly alkaline during the addition stage. The reaction mixture was stirred overnight and the dark solid filtered off and dried. The azo dye was purified by column chromatography over alumina and eluting with toluene, giving (**4c**) as dark blue crystals (0.19 g, 51%). Found: C, 68.85; H 4.00; N, 18.35%; M^+ 381. $C_{22}H_{15}N_5O_2$ requires C,69.28; H,3.96; N,18.36%; M 381.

2.8. *3,5-Dinitrothienylazo dye* **4d**

Sodium nitrite (0.14 g, 0.002 mol) was dissolved in concentrated sulfuric acid (3 ml) by heating to 60°C and the solution was then cooled to 0–5°C. 2-Amino-3,5-dinitrothiophene (0.1 g, 0.0005 mol) was added to the acidic solution and stirred for 10 min in an ice bath. The resultant diazonium solution was slowly added to 9,10-dimethylacridinium methylsulfate (0.16 g, 0.0005 mol) in water (25 ml), whilst adding dilute sodium hydroxide solution to maintain the alkalinity of the reaction solution. The mixture was stirred for 24 h and the resultant solid filtered off and dried. This was chromatographed over alumina in toluene, affording pure (**4d**) as a dark blue solid (8 mg, 4%). Mass spectrum: found $m/z = 407$; $C_{19}H_{13}N_5O_4S$ requires $M = 407$.

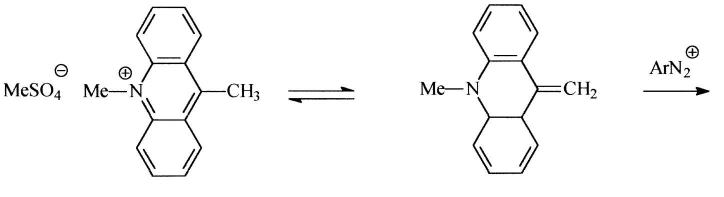
3. Results and discussion

3.1. *Synthesis of dyes* **4a–d**

Although 10-methyl-9-methylene-9,10-dihydroacridine **1** can be generated from a 9,10-dimethylacridinium salt (e.g. **5**) by deprotonation with bases, it is more convenient to use the salt itself for the synthesis of derived dyes, and to effect deprotonation in situ. The salt **5** can be prepared by heating diphenylamine and zinc chloride in acetic acid at 220°C [1], followed by methylation of the dihydroacridine with dimethyl sulfate [3]. It was found that diazonium ions coupled readily to **5** in water (Scheme 1), provided a neutral or alkaline pH was maintained.

Thus, in the case of the 4-*N,N*-dimethylamino- and 4-nitro-phenylazo derivatives **4a** and **4b**, the appropriate diazonium tetrafluoroborate salt could be added directly to an aqueous solution of **5** at neutral pH, when coupling occurred at room temperature over a period of about one hour. In the case of the 2-cyano-4-nitrophenylazo- and 3,5-dinitrothienylazo-derivatives **4c** and **4d** respectively, solutions of the diazonium salts were prepared from the amine and nitrosylsulfuric acid, and sodium hydroxide was used to neutralize excess sulfuric acid during the coupling reaction. It was found better to use a large excess of the diazonium ion in the case of **4d** as the diazonium proved very unstable under these reaction conditions. Even with a twofold excess of the ion, **4d** could only be isolated in very low yield.

The crude products generally required purification by column chromatography (toluene over alumina), and the observed yields generally reflected the efficiency of the diazonium ion as a coupling reagent, i.e. its electrophilicity. Thus **4b** and **4c** were isolated in ca. 50% yield, whereas the weakly electrophilic 4-*N,N*-dimethylaminobenzene diazonium ion afforded **4a** in only 24% yield. As noted previously, **4d** could only be isolated in very low yield, even though the 3,5-dinitrothienyldiazonium



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Scheme 1.

ion is a powerful electrophile, reflecting the instability of the diazonium ion towards hydrolysis.

3.2. *Visible absorption spectroscopic properties of dyes* 4

The neutral dyes **4** are typical donor–acceptor azo dye chromophores, and thus, given the known powerful electron donating strength of the dihydroacridine residue, one might expect exceptionally long wavelength absorption in comparison with related azo dyes derived from *N,N*-dialkylanilines. In addition, the donor-acceptor character of the chromophoric system suggests that the λ_{max} values should show a bathochromic shift as the electron withdrawing strength of the diazo component increases. These two expectations were realised in practice, as indicated by the data presented in Table 1. Thus the powerful bathochromic effect of the dihydroacridine system is indicated by the fact that the simple 4-nitrophenylazo dye **4b** is blue in ethanol, with a λ_{max} of 590 nm. This may be compared, for example, with 4-(4′-nitrophenylazo)-*N,N*-dimethylaniline, which is orange-red in ethanol ($\lambda_{max} = 478$ nm).

The general shift of λ_{max} to longer wavelength as the electron acceptor strength of the diazo component increases is shown clearly with dyes **4a–c**, where λ_{max} values of 561, 590 and 650 nm are observed respectively. However, dye **4d** appears to be exceptional, and this dye absorbs at 610 nm in ethanol, some 40 nm to shorter wavelengths than dye **4c**.

Table 1
Light absorption properties of the dyes **4** in ethanol

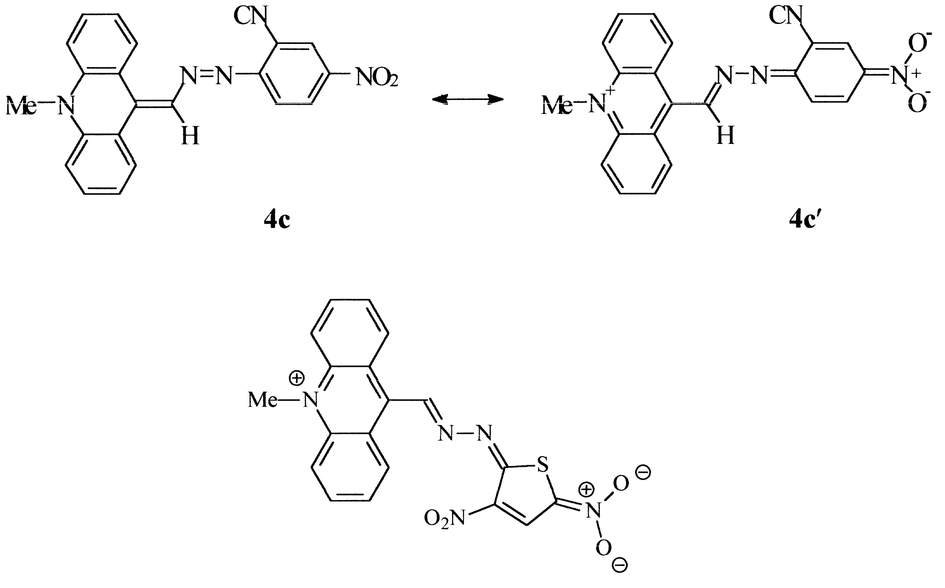
Dye	λ_{max}(nm)	ϵ_{max} (l mol^{-1} cm^{-1})
4a	561	22,000
4b	590	25,000
4c	650	25,000
4d	610	20,000

The unexpectedly hypsochromic nature of the dinitrothienyl dye **4d** may be due to the combined powerful electron donor and acceptor effects of the dihydroacridine and dinitrothiophene systems respectively, resulting in a chromophore that has passed the isoenergetic point [4,5]. This means that whereas the electronic structure of **4c** is probably almost halfway between the two contributing resonance canonical forms **4c** and **4c′** (Scheme 2), and so has near the optimum bathochromic shift, dye **4d** has a structure best approximated by **4d′** (Scheme 2), and the loss of electronic symmetry results in a hypsochromic shift of the visible band.

3.3. *Halochromic properties of* 4

It was noted that when TLC analysis of **4b** was attempted on a silica substrate, the sample spot rapidly changed from blue to deep red, and the resultant red compound could not be eluted with dichloromethane. The colour change could be reversed in the presence of bases, and it was concluded that the phenomenon was due to the high basicity of the dye, the silica inducing protonation to give the cation **6b** (Scheme 3).

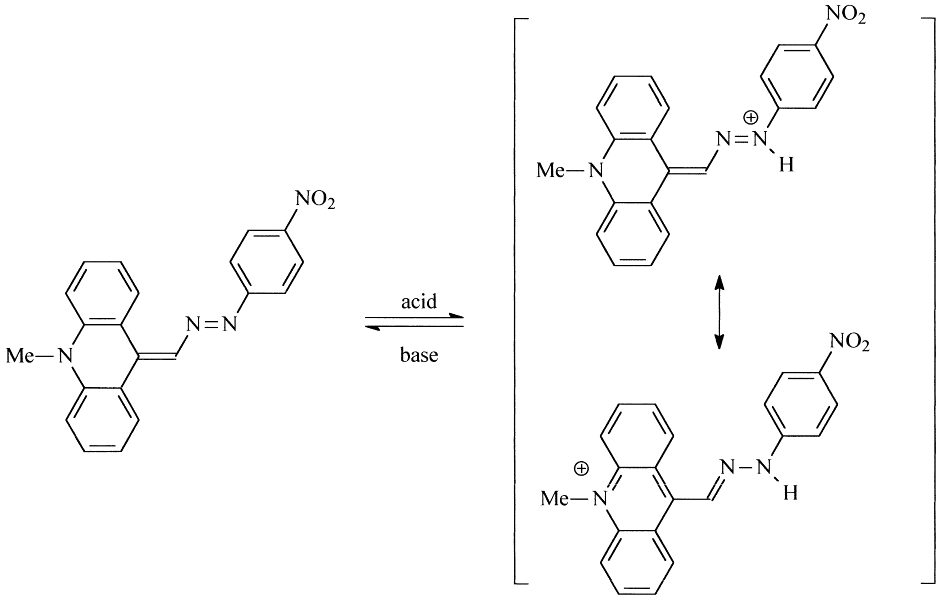
This was confirmed by visible absorption spectroscopy, when gradual addition of acid to a solution of **4b** resulted in a shift of the visible peak from 590 nm to 528 nm, with a clear isosbestic point at 550 nm (Fig. 1). Thus dye **4b** is *negatively halochromic*, i.e. protonation causes a hypsochromic displacement of the absorption band.



4c **4c′**

4d′

Scheme 2. Resonance forms for dyes **4c** and **4d**.



4b **6b**

Scheme 3.

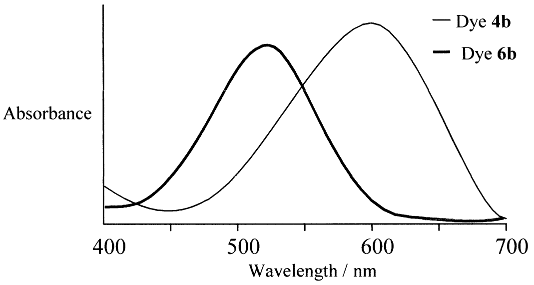


Fig. 1. Absorption spectrum of azo dye **4b** and its protonated form **6b** in ethanol.

Negative halochromism is a relatively rare phenomenon in azo dyes, postive halochromism being more usual [6]. The former is usually observed when the dye contains an exceptionally powerful acceptor residue or an exceptionally powerful donor system [7], and as **4b** contains both types of residue it is not surprising that it shows this effect to such a pronounced degree.

The observed protonation of **4b** on silica suggests that the dye possesses an unusually high pK_b value. Therefore, to investigate the protonation characteristics of dyes **4** in general, approximately 2×10^{-5} M solutions of the dyes in water containing the minimum quantity of acetone to effect complete dissolution were prepared. Samples of the solutions were then taken and their pH values adjusted by adding small amounts of very dilute hydrochloric acid, the pH values of the solutions being measured with a calibrated digital pH meter. The absorption spectra of the solutions were then measured. By monitoring at the λ_{max} of the neutral dye, where the protonated species has negligible absorbance, it was then possible to determine the pH at which the dye was 50% protonated, i.e. the pK_b value. A typical example is shown in Fig. 2 for dye **4c**, which had a pK_b value of ca. 5.0. The pK_b values for dyes **4b-d** with strong electron withdrawing groups range from 4.6 to 5.0 (Table 2), and are significantly higher than those of similarly substituted aminoazobenzene dyes. This reflects the gain in stability of the system when it assumes the aromatic character of the acridinium ion (see for example **6b** in Scheme 3). The most striking visual colour change was observed for **4b** (blue to red), making it a particularly useful pH indicator, although the colour changes for **4c** (cyan to violet) and **4d** (blue to to purple) were also sufficiently pronounced for such an application.

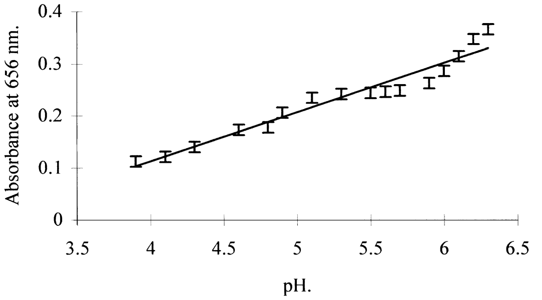


Fig. 2. Plot of absorbance at 656 nm (λ_{max} of the neutral dye) against pH for dye **4** (solvent water with a trace of acetone).

Table 2
Halochromic properties of dyes **4** in ethanol

Dye	λ_{max} (nm) (neutral)	λ_{max} (nm) (protonated)	$\Delta\lambda$ (nm)	pK_b
4a	561	537	−24	8.2
4b	590	528	−62	5
4c	650	588	−62	4.6
4d	610	558	−52	4.9

Dye **4a**, which contains the strong *N*,*N*-dimethyl-amino electron donor group, not surprisingly had an exceptionally high pK_b value (8.2), which meant that when synthesised by coupling at neutral pH it was actually isolated in its protonated form. Unfortunately, the observed colour change accompanying protonation of this dye (red to purple from low pH to higher pH), is less pronounced than for other dyes in the series, and thus **4a** has only limited value as a pH indicator.

4. Conclusions

10-Methyl-9-methylene-9,10-dihydroacridine couples with diazonium ions to give azo dyes **4**, which show an unusually high bathochromicity. This is exemplified by the simple 4-nitrophenylazo derivative **4b**, which is blue. The chromophoric system of **4** can be considered as donor–acceptor in character, with the dihydroacridine residue functioning as a powerful electron donor. Increasing the acceptor strength of the arylazo component thus provides the expected progressive bathochromic shift, but the isoenergetic point is soon reached, and dye **4d** containing the powerful 3,5-dinitro-thienyl acceptor residue absorbs at shorter wavelengths than then 2-cyano-4-nitrophenyl dye **4c**. Thus, it seems unlikely that near-infrared absorbing dyes of this class could be made by simple modification of the electron withdrawing properties of the diazo component, unless a significant increase in conjugation length of the chromophore was also introduced. The dyes **4** are readily protonated, having pK_b values in the range 4.6–8.2. Protonation results in a large hypsochromic shift of the absorption band, which reflects the powerful electron donating characteristics of the dihydroacridine residue. The large colour changes observed with certain of the dyes makes them of potential value as pH indicators.

Acknowledgements

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