



Synthesis and Electronic Spectral Characteristics of Some New Azo Merocyanine Dyes

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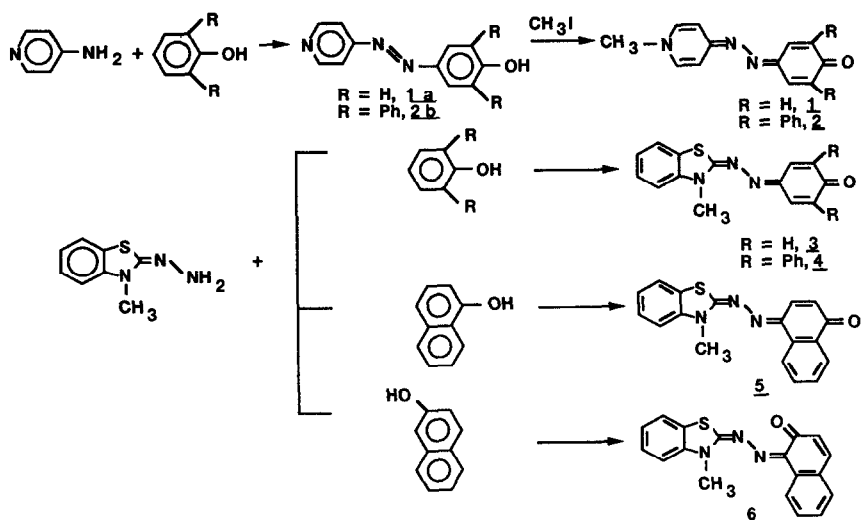
The synthesis of new solvatochromic azo merocyanine dyes (1–6) is described. The preparations involve coupling of 4-aminopyridine with appropriate phenols and subsequent methylation by methyl iodide. N-Methylbenzothiazolylazo-4'-benzoquinone (3) and N-methylbenzothiazolylazo-(3',5'-diphenyl)-4'-benzoquinone (4) were synthesised by coupling with phenols. In an alternative route, N-methylbenzothiazolinone hydrochloride (MBTH) was converted via the sulphonyl hydrazone to the azo sulphone, followed by coupling with various phenols to yield 3 and 4. Naphthoquinones were coupled to MBTH to give N-methylbenzothiazolyl-4'-naphthoquinone (5) and N-methylbenzothiazolyl-2'-naphthoquinone (6). The UV-Vis spectra of the six dyes (1 to 6) were recorded in 29 solvents and their λ_{max} values and molar extinction coefficients (ϵ) are presented. The effect of structural change on the electronic spectra, on replacement of the $-\text{CH}=\text{CH}-$ bridge by $-\text{N}=\text{N}-$ in merocyanines, is discussed.

1 INTRODUCTION

Merocyanine dyes are an important class of compounds due to their diverse applications in various fields, such as neurophysiology,^{1,2} electrochromism,³ nonlinear optics,⁴ new material technology,^{5–8} solvatochromism^{9,10} and photochromism.¹¹

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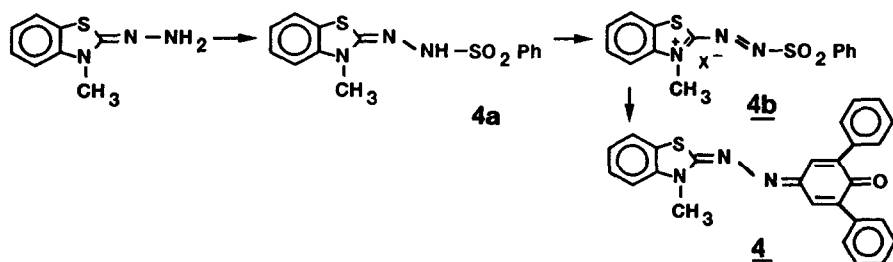
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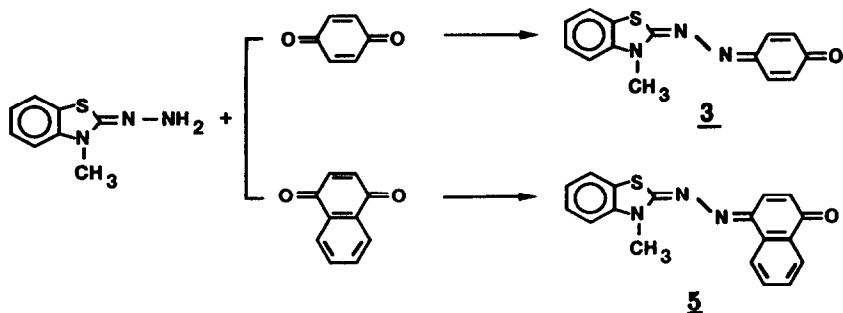
Scheme 1. 4-Aminopyridine is coupled with phenols to form **1a** and **2a**, which on methylation give **1** and **2**. MBTH is coupled with various phenols to give products **3–6**.

Solvatochromism is manifested as a pronounced change in the position, intensity, and shape of an absorption band when a solute is dissolved in solvents of varying polarity. A bathochromic (red) shift and a hypsochromic (blue) shift with increasing polarity are called positive and negative solvatochromism, respectively. A change from bathochromic to hypsochromic, or vice versa, with increase in solvent polarity, is termed reverse solvatochromism. Studies on solvatochromism of merocyanines have mostly focused on stilbazolium-type dyes.^{12–16}

We report here the electronic spectral data of the merocyanine dyes **1–6**. Recently we reported a new solvent polarity scale, the π_{azo}^* scale, based on the averaged spectral characteristics of the new azo merocyanine dyes in different solvents.¹⁷ We also reported interesting spectral behaviour concerning a reverse solvatochromism of these dyes.¹⁸ We now report the syntheses and electronic spectral characteristics of these azo merocyanine



Scheme 2. MBTH is converted to sulphonyl hydrazone **4a** to give azo sulphone **4b**. Azo sulphone is then coupled with 2,6-diphenylphenol to give **4**.



Scheme 3. MBTH is coupled with quinones to give products 3 and 5.

dyes. The present studies form an extension of our previous studies on azo and azoxy dyes.^{19–27}

Compounds **1** and **2** were prepared by coupling 4-aminopyridine with appropriate phenols to give pyridylazophenols which were subsequently methylated using methyl iodide as outlined in Scheme 1. Compounds **3–6** were synthesised via two pathways, Schemes 1–3. *N*-Methylbenzothiazolinone hydrochloride (MBTH) was coupled with phenols (1:10) to yield *N*-methylbenzothiazolyl phenols (Scheme 1). In a different pathway, MBTH was converted via the sulphonyl hydrazone to the azo sulphone, which was subsequently coupled with different phenols (1:1) to give the desired products. Scheme 3 shows the coupling of quinones to MBTH to yield compounds **3** and **5**.

Preparation of compounds **1**, **3**, **5** and **6** was based on literature reports.²⁸ The new azo merocyanines **2a**, **2**, **4a**, **4** were synthesised using modified methods.

2 EXPERIMENTAL

2.1 General

N-Methylbenzothiazolinone hydrazone hydrochloride (MBTH) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone urea (DMPU) from Fluka were used without purification. Pyridine derivatives, phenols and quinones were obtained from Aldrich Chemical Co. Silica gel chromatogram plates (Kodak 13181 coated with fluorescent indicator) were used for thin layer chromatography (TLC). Precoated TLC plates (silica 60 μm without fluorescent indicator, 0.25 mm thickness) from BDH were used for preparative TLC. BDH silica 60 μm , 230–400 mesh ASTM, was used for liquid chromatography (LC). Prepacked columns (240 mm, 310 mm and 440 mm; 40–63 μm) were for used medium-pressure liquid chromatography

(MPLC) (1400–2100 kPa). Elemental analyses were performed by the Canadian Microanalytical Service (**2a**, **4**, **6**), Guelph Laboratories (**3**), and Galbraith Laboratories Inc. (**2**). Melting points were determined on a Fisher–Jones apparatus and are reported uncorrected in degrees Celsius (°C).

2.2 4-(*p*-Hydroxyphenylazo)pyridine (**1a**)

A solution of NaNO₂ (8.0 g) in H₂O (40 ml) was added to freshly distilled phenol (12.0 g) in 10% aq. NaOH (90 ml) and cooled to 0°C. The resulting solution was added slowly with stirring to a solution of 4-aminopyridine (12.0 g) in aq. HCl (50 ml conc. HCl in 32 ml H₂O). Following the addition, the pH was adjusted to 6, the precipitate was filtered and recrystallised from ethanol to give reddish yellow crystals of **1a**, yield 23%, m.p. 256–257° (dec.), lit. m.p. 252–253°C.^{29,30}

2.3 4-*N*-Methyl-(4'-hydrazobenzoquinone)pyridone (**1**)

4'-Hydroxyphenylazopyridine (**1a**) (1.0 g, 5 mmol) was dissolved in 150 ml *N,N*-dimethylacetamide (freshly distilled), methyl iodide (4.1 g, 30 mmol) was added and the mixture was stirred at 40°C for 2 days. The reaction was followed spectrophotometrically and by TLC. After 2 days, the reaction mixture was concentrated to 40 ml and product was precipitated with 50 ml water. The precipitate (1.0 g) was dissolved in alkaline ethanol (65 ml 10% NaOH/65 ml EtOH) and extracted with chloroform using a continuous extractor. The pink aqueous layer slowly turned pale as the chloroform layer became intense purple. The organic layer was concentrated and the product mixture was separated by column chromatography with MeOH/CHCl₃ (5:1, v/v). The column showed five well separated zones: yellow ring, brown band, reddish orange ring, purple zone and a faint yellow ring. The purple band was separated, concentrated and recrystallised from toluene to give **1**, yield 27%, m.p. 215–216°, lit. m.p. 218°C.³¹

2.4 4-(4'-Hydroxy-3',5'-diphenyl)phenylazopyridine (**2a**)

A solution of 10 g (40 mmol) of 2,6-diphenylphenol in 1 liter of ethanol and a solution of 10 g borax and 34 g NaOH in 500 ml water were combined (solution A) and kept at 0°C. Then, sodium nitrite (2 g; Analar) in 10 ml water and 2.87 g (30 mmol) of 4-aminopyridine (freshly recrystallised from hot toluene) in 4M-HCl (45 ml) were mixed quickly at 0°C (20 s). After 30 s stirring, the mixture was quickly poured into solution A resulting in a bright red mixture (Solution B). Solution B was acidified to pH 6. At this pH, the solution turned turbid yellow with the formation of a yellow precipitate. The

precipitate was filtered and recrystallised from hot toluene with the aid of decolourising carbon. The product obtained was a reddish orange powder of (4'-hydroxy-3',5'-diphenyl)phenylazopyridine(**2a**), yield 22%, m.p. 270–272°.

Calcd for $C_{23}H_{17}N_3O$: C, 78.63; H, 4.84; N, 11.97.

Found: C, 78.57; H, 4.94; N, 11.47%.

2.5 4-N-Methyl(4'-hydrazo-3',5'-diphenylbenzoquinone)pyridone (**2**)

Freshly distilled *N,N*-dimethylacetamide (150 ml) was preheated to 38–40°C and 4-(4'-hydroxy-3',5'-diphenyl)phenylazopyridine (**2a**) (1.0 g, 5 mmol) was added and the mixture stirred until all the substance dissolved. Freshly distilled MeI (2.0 g) was added and the reaction mixture was stirred for 4 days at 38–40°C. The reaction was monitored spectrophotometrically and by TLC. The reaction mixture was concentrated to 40 ml. Addition of 50 ml distilled water resulted in a greyish brown precipitate which was filtered (1.2 g). This precipitate was dissolved in an alkaline ethanol solution (75 ml 10% NaOH and 100 ml ethanol) by agitating for one day. The product from the aqueous solution was extracted into chloroform using a liquid–liquid extractor by downward displacement. This extraction took 3 days to complete during which time the purple-coloured aqueous solution turned pale and the organic solution (chloroform) turned bright purple. The chloroform extract was passed down a column of silica and the purple zone (sixth from the bottom of the column) was eluted with MeOH/ $CHCl_3$ (3:5, v/v). This purple solution was then concentrated to 1 ml and further separated using HPLC. The eluting solvent mixture used was ethanol/toluene (3:5, v/v). The chromatogram nicely separated into four distinct bands: brown, orange, purple and yellow. The purple band was eluted and concentrated to give a bluish grey powder. The product was purified by dissolving in toluene (0.5–1 ml) and triturating with petroleum ether (0.5–1 ml), which afforded a shiny bluish brown powder of **2**, yield 6%, m.p. 278–280°.

Calcd for $C_{24}H_{19}N_3O$: C, 78.87; H, 5.24; N, 11.50.

Found: C, 78.71; H, 5.05; N, 10.97%.

2.6 N-Methylbenzothiazolylazo-4'-benzoquinone (**3**)

This compound was prepared in two ways (Schemes 1 and 3).

2.6.1 Method 1

MBTH was coupled with phenol via oxidative coupling under nitrogen. A flask equipped with a nitrogen inlet was charged with 38 mg (175 μ mol) of MBTH in 10 ml 50% methanol, 1.25 g (10 mmol) of freshly distilled phenol

in 15 ml 50% methanol and 30 ml of 9.2 Universal buffer solution (50 ml 0.025M- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 0.9 ml 0.1M-NaOH, and 49.1 ml distilled water). Aqueous solution (100 ml) containing 845 mg (2 mmol) $\text{K}_4\text{Fe}(\text{CN})_6$ and 6.92 g (20 mmol) $\text{K}_3\text{Fe}(\text{CN})_6$ was added slowly. The reaction solution turned raspberry-red in colour. After 30 min, the reaction mixture was treated with 100 ml of chloroform. The desired product was extracted into the chloroform layer which was rotary-evaporated *in vacuo*. The residue was recrystallised from *n*-amyl alcohol giving purple needles of **3**, yield 27%, m.p. 228–230°, lit. m.p. 229–230°C.³²

2.6.2 Method 2

MBTH was coupled with 1,4-benzoquinone directly. 216 mg (3 mmol) of freshly recrystallised *p*-benzoquinone (from petroleum ether) in 15 ml water and 696 mg (3.2 mmol) of MBTH in 10–20 ml H_2O were combined in a 125 ml Erlenmeyer flask which was wrapped in aluminium foil and kept for 24 h at room temperature. A purple-coloured precipitate was formed which was filtered and recrystallised from 35 ml hot amyl alcohol to give purple-coloured needles of **3**, 61% yield, m.p. 228–230°, lit. m.p. 230–231°C.³³

Calcd for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{OS}$: C, 62.41; H, 4.12; N, 15.60; S, 11.91.

Found: C, 62.83; H, 4.56; N, 15.50; S, 11.17%.

2.7 *N*-Methylbenzothiazolylazo-(3',5'-diphenyl)-4'-benzoquinone (**4**)

This compound was prepared via two methods. In method 1 (Scheme 2), MBTH was first converted to azo sulphone (**4b**) via the sulphonyl hydrazone (**4a**). Subsequently, in step 3, the azo sulphone was coupled to 2,6-diphenylphenol to give the desired product (**4**).

2.7.1 Method 1: via azo sulphone

Step 1: formation of sulphonyl hydrazone (4a). To a stirred mixture of MBTH (1.46 g) in 10 ml *N*-methylpyrrolidone (NMP), ZnO (0.3 g) and benzenesulphonyl chloride (1.5 g) in 25 ml NMP were added under a nitrogen atmosphere and the mixture was heated for 90 min at 90–100°C. The reaction mixture, which was turbid white before heating, turned yellow and finally reddish brown during the course of reaction. The reaction mixture was acidified to pH 5, when precipitation occurred. The precipitate was filtered and purified by dissolving in alkaline methanol and reprecipitating with conc. HCl to pH 5. The reaction yielded 23% of a brown product, **4a**, m.p. 220–221°, lit. m.p. 220–221°C.³⁴

Step 2: formation of azo sulphone 4b from sulphonyl hydrazone (4a). The sulphonyl hydrazone (**4a**) (150 mg) was stirred into a solution containing

10–20 ml H₂O and aqueous fluoroboric acid (8 ml 45% HBF₄ in 10 ml H₂O) and the mixture stirred for 20 min to ensure dissolution of **4a**. Pb(OAc)₄ (1.0 g) in 15 ml glacial acetic acid was added to the reaction mixture and the solution immediately turned brown. Concentrated HNO₃ (20 ml) was added slowly dropwise into the reaction mixture. The reaction vessel was kept in an ice–water bath during the addition of HNO₃. The mixture was stirred for 15 min and diluted with 20–30 ml water during which a brown–yellow precipitate was formed. The precipitate was filtered, washed with 5 ml aq. HBF₄, dried *in vacuo* and purified by dissolving 25 ml acetonitrile and triturating with 15–20 ml diethyl ether. The reaction yielded 92 mg (61%) of a bright yellow powder, the azo sulphone **4b**, m.p. 182–184°, lit. m.p. 182–185°C.³⁴

Step 3: coupling of azo sulphone (4b) with 2,6-diphenylphenol. The azo sulphone (**4b**) (400 mg; 1 mmol), and 2,6-diphenylphenol (500 mg; 2 mmol) were dissolved in a mixture of 40 ml acetone and 10 ml 2M-NaOH. The solution turned from yellow to purple. The solution was boiled for 10 min during which time a pink precipitate was formed. The precipitate was filtered and recrystallised from 50 ml hot chlorobenzene to give purple crystals of **4** (20%), m.p. 320–322°.

2.7.2 Method 2: oxidative coupling of MBTH with 2,6-diphenylphenol

A solution of K₃Fe(CN)₆, 7.73 g (11 mmol), in 100 ml (50%) aqueous methanol (solution A) and 10 ml 25% NH₄OH (solution B) were prepared separately. Solutions A and B were added to a mixture of 1.42 g (6 mmol) MBTH and 5.0 g (6 mmol) 2,6-diphenylphenol in 100 ml 70% methanol. On gentle warming a bright red precipitate was formed. On dilution with 250 ml water, the amount of precipitation increased. After 15 min the solution was filtered and the precipitate was dried *in vacuo*. The dried precipitate was recrystallised with 200–250 ml hot chlorobenzene yielding purple crystals of **4** (1.35 g; 62%), m.p. 319–321°.

Calcd for C₂₆H₁₉N₃OS: C, 74.08; H, 4.55; N, 9.97; S, 7.60

Found: C, 73.73; H, 4.52; N, 9.89; S, 8.13%.

2.7.3 N-Methylbenzothiazolyl-4'-naphthoquinone (5)

The synthesis was carried out as described above but substituting 0.81 g (5 mmol) α -naphthol for 2,6-diphenylphenol. The final precipitate (2.0 g) was recrystallised from 150–200 ml hot glycol monomethyl ether to give a red powder, **5** (60 mg, 33%), m.p. 260–270°, lit. m.p. 274°C.³²

2.7.4 N-Methylbenzothiazolyl-2'-naphthoquinone (6)

As described above, 0.80 g (5 mmol) of β -naphthol was used to prepare the

title compound. The dried precipitate was recrystallised from 200–250 ml hot chlorobenzene to give 50 mg (32% yield) of **6**, m.p. 243–245°, lit. m.p. 243–245°C.³²

Calcd for $C_{18}H_{13}N_3OS$: C, 67.71; H, 4.07; N, 13.16; S, 10.03.

Found: C, 67.26; H, 4.08; N, 13.08; S, 9.69%.

2.8 UV-Vis studies

The solvents used were of spectrometric grade quality whenever possible. The following spectrometric solvents were used without further purification: hexanes, chlorobenzene, ethyl acetate, monoglyme, methyl acetate, ethyl acetate, 1,2-dichloromethane, benzonitrile, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, 1-propanol, and 1,4-dioxane (Aldrich Chemical Co.); toluene, benzene, chloroform, 2-butanone, acetone, dimethyl sulphoxide, acetonitrile, methanol, ethanol and cyclohexane (BDH Chemicals). Diethyl ether, nitrobenzene, pyridine, and nitromethane (Aldrich) were distilled before use. Hexamethylphosphoramide (HMPA) and *N,N*-(dimethylpropylene)urea (DMPU, Fluka) were used without further purification.

The above solvents were chosen from a broad spectrum ranging from 32.6 to 63.1 in their E_T scale (Dimroth and Reichardt's solvent polarity scale) and grouped into three sets as follows: set 1 (E_T 30–40) solvents 0–10; set 2 (E_T 41–50); set 3 (E_T 51–65), solvents 23–27.

Due to the varying solubility of the azo merocyanines **1–6** in the above solvents, a cosolvent was chosen in each set to prepare stock solutions: chloroform in set 1, acetone in set 2, and ethanol in set 3. Aliquots of 5 μ l of the stock solution (10 mm) were added to 2.0 ml of solvent placed in a quartz cuvette and the UV-Vis spectra were scanned over the range 320–780 nm using a Perkin-Elmer Lambda 5 spectrophotometer equipped with a thermostated cell holder. The presence of the cosolvent (0.25%) did not alter the spectra detectably. The spectrometer was routinely calibrated and checked for wavelength accuracy by means of holmium and didymium filters before and after measurements. All spectral measurements were performed at 25°C.

3 RESULTS AND DISCUSSION

3.1 Synthetic procedures

The synthesis of azo merocyanine dyes was successful though yields were not high (20–50%) due to the formation of several side products of unknown identity. Fortunately most of the components in a product mixture showed

well-separated brightly coloured bands on a liquid column chromatogram. The azo merocyanines were generally isolated from purple or dark blue bands under the experimental conditions used.

The coupling reaction of 1,4-benzoquinone with MBTH (Scheme 3) resulted in higher yield of the desired product **3** than the oxidative coupling reaction of phenol to MBTH (Scheme 1). Based on the experimental method and yield, oxidative coupling of MBTH with phenols (Scheme 1) was found to be a more efficient pathway than via formation of the azo sulphone (Scheme 2).

3.2 Electronic spectral characteristics of azo merocyanines

Earlier studies on the spectral properties of dyes have focused on azo and stilbazolium-type dyes.^{12–16} Reports of spectral data of azo merocyanines in various solvents are fairly limited.³⁵ Although several of these systems are known, their spectral properties are not well documented and few conclusions can be drawn concerning the effect of the hetero atoms on absorption spectra. Published studies of structural effects on the visible spectra of various azo dyes have concentrated mainly on dyes derived from substituted aniline derivatives obtained by coupling with dialkylanilines, where the intense visible band is due to the first $\pi\text{--}\pi^*$ transition and not to the relatively weak $n\text{--}\pi^*$ band intrinsic to the --N=N-- group.¹⁶ Since there are abundant spectral data available in the literature on stilbazolium dyes, we have compared the spectral data of the azo merocyanines with the iso- π electronic merocyanine dyes. We have found interesting trends concerning the nature of the solvatochromism in these molecules and we present the treatment below.

Our investigation of the electronic spectral characteristics of azo merocyanines has focused on the following: (a) determining the spectral shifts with varying solvent polarity; (b) evaluating the influence of the azo moiety on the solvatochromism of merocyanines; and (c) formulation of a solvent polarity scale by a multiple parameter approach.

One hundred and seventy-two spectra of the six synthesised compounds in 29 solvents were recorded in the region between 320 to 780 nm. Representative spectra are shown in Figs 1–3. Wavelength maxima (λ_{max}) and extinction coefficients (ϵ) are tabulated in Table 1. All the solutes displayed a bathochromic shift (red shift), thus exhibiting positive solvatochromic behaviour. The longest-wavelength bands of the six solutes are plotted in Fig. 4. It is seen that the six solutes show a similar trend with respect to the rise and fall in λ_{max} with various solvents. Of the six solutes **2** shows the longest wavelength maximum, 580 nm in dimethyl sulphoxide. A solvent change from hexanes to dimethyl sulphoxide caused a bathochromic

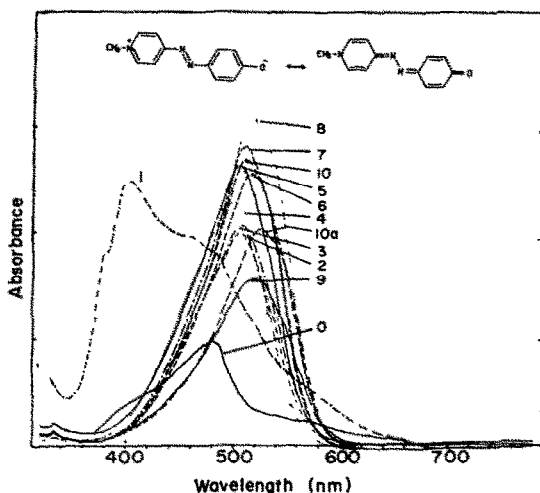


Fig. 1. Absorption spectra of 4-*N*-methyl-(4'-hydrazobenzoquinone)pyridone (1) in solvents 0–10a. 0 Hexanes; 1 Cyclohexane; 2 Toluene; 3 Benzene; 4 Diethyl ether; 5 1,4-Dioxane; 6 Chlorobenzene; 7 Ethyl acetate; 8 Monoglyme; 9 Chloroform; 10 Methyl acetate; 10a 1,2-Dichloroethane.

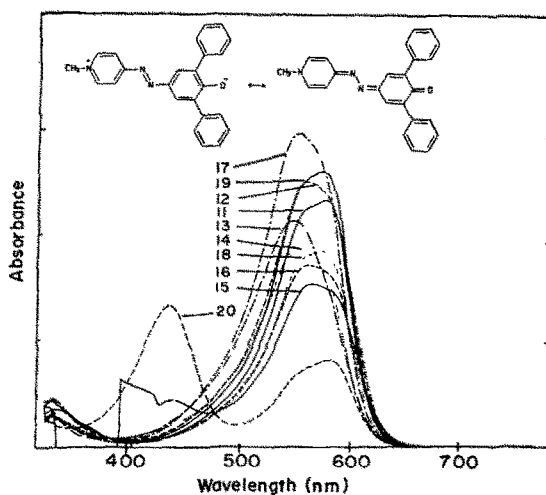


Fig. 2. Absorption spectra of 4-*N*-methyl-(4'-hydrazo-3',5'-diphenylbenzoquinone)pyridone (2) in solvents 11–20. 11 Hexamethylphosphoramide; 12 Pyridine; 13 Dichloromethane; 14 2-Butanone; 15 Nitrobenzene; 16 Benzonitrile; 17 Acetone; 18 Dimethylacetamide; 19 Dimethylformamide; 20 Dimethyl sulphoxide.

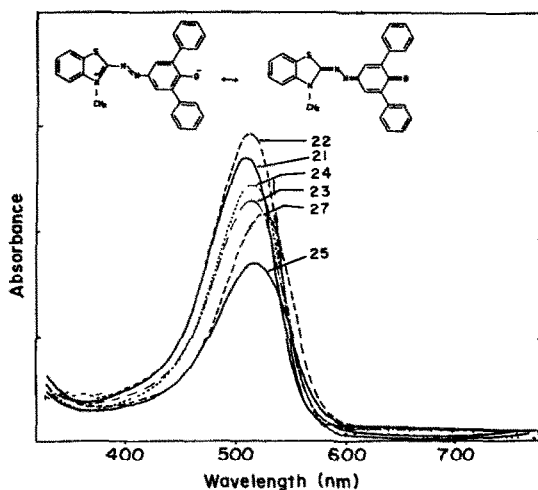


Fig. 3. Absorption spectra of N-methylbenzothiazolylazo-(3',5'-diphenyl)-4'-benzoquinone (4) in solvents 21-27. 21 Acetonitrile; 22 Nitromethane; 23 n-Propanol; 24 Ethanol; 25 Methanol; 26 Water; 27 DMPU.

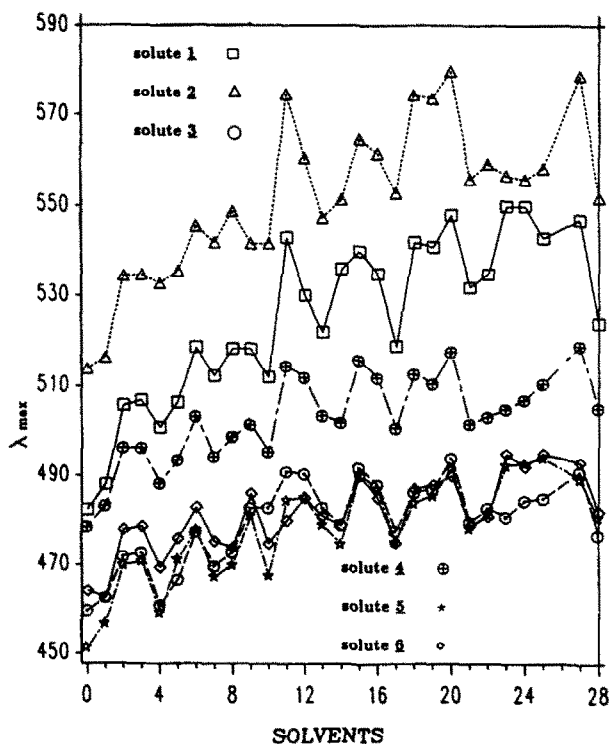


Fig. 4. Comparison of maxima of long-wavelength absorptions for solutes 1-6 in solvents 0-28.

11	HPMA	543	61 400	575	76 600	484	37 500	515	52 100	480	17 500	480	15 300
12	Pyridine	531	53 000	560	85 900	485	43 800	512	63 600	486	17 200	486	15 000
13	Dichloromethane	522	44 300	547	73 100	479	33 200	504	53 600	482	17 600	482	15 600
14	2-Butanone	537	32 900	551	63 100	474	39 100	502	65 600	477	17 800	477	16 900
15	Nitrobenzene	540	38 400	565	51 500	490	59 000	516	62 100	490	19 300	490	17 900
16	Benzonitrile	537	50 400	561	58 400	487	39 100	512	152 300	480	11 920	480	18 900
17	Acetone	521	52 800	553	91 300	475	38 900	501	179 100	478	11 970	475	21 600
18	<i>N,N</i> -Dimethylacetamide	542	45 900	574	62 700	484	35 700	512	159 700	486	19 300	487	20 500
19	DMF	542	59 000	573	89 500	486	37 900	513	158 900	487	20 900	488	21 700
20	DMSO	408	19 500	433	44 900	492	42 700	518	189 600	494	25 500	491	20 800
		548	6 700	580	27 400								
21	Acetonitrile	532	29 900	556	54 400	478	36 500	501	165 300	479	17 600	482	23 600
				559	14 300								
22	Nitromethane	535	39 600	416	39 100	482	36 400	503	42 300	483	14 300	480	12 700
		360	46 500	367	20 100	359	5 600	359	3 100				
23	1-Propanol	550	41 400	557	55 500	493	36 600	505	153 700	481	27 200	520	32 100
24	Ethanol	550	27 400	556	30 400	493	36 300	507	48 700	484	18 500	493	21 000
25	Methanol	543	33 800	559	71 300	494	37 100	510	40 900	485	23 200	495	27 100
26	Water	531	36 300	559	40 900	509	8 700						
27	DMPU	547	69 800	579	82 300	489	40 000	520	86 700	491	49 100	493	52 200

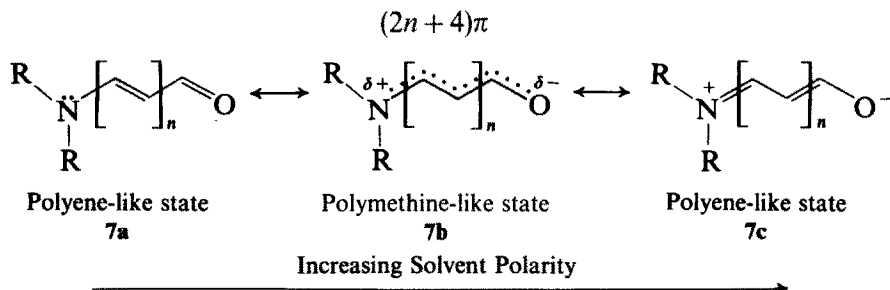
^a Abbreviations: HMPA, hexamethylphosphoramide; DMF, dimethylformamide; DMSO, dimethyl sulphoxide; DMPU, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone urea.

shift of 65 nm in its longest-wavelength band. For all the solutes, DMSO shows the longest-wavelength maxima.

The solvent effect on electronic absorption spectra, resulting from electronic transitions, is primarily dependent on the chromophore and the nature of the transition ($\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and charge-transfer absorption). The electronic transitions of particular interest in this respect are $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and charge-transfer absorptions. A qualitative interpretation of solvent shifts is possible by considering the following factors as guides:^{9,10}

- the momentary transition dipole moment present during the optical absorption;
- the difference in permanent dipole moment between the ground state and the excited state of the solute;
- the change in ground-state dipole moment of the solute induced by the solvent;
- the Franck–Condon principle.

For strongly solvatochromic dyes the observed solvent shifts cannot be explained only in terms of a change in the permanent dipole moment on electronic transition ($\mu_g \neq \mu_e$). The effect of the surrounding solvent cage ($\mu_g \rightarrow \mu'_g$) on the ground state dipole moment of the solute should also be taken into consideration.^{36–42} The dipolar solute molecules cause an electronic polarisation of the surrounding molecules, creating a so-called reaction field, which affects the dye's ground-state dipole moment μ_g .⁴² That is, the interaction of the dipolar solute molecules with this induced reaction field, due to the total dipole moment (actual and induced) of the solvent molecules, may cause an alteration of the electronic structure of the chromophore. For meropolymethine dyes, such as the positively solvatochromic merocyanine **7** described below, this implies that increasing solvent polarity should shift the electronic structure from a more polyene-like state (**7a**), to a more polymethine-like state (**7b**), and eventually to **7c**, which is also a polyene-like state:



Therefore, a chromophore with a polyene-like electronic structure (**7a**) will exhibit a bathochromic shift with increasing solvent polarity (positive solvatochromism), whereas a chromophore with a polymethine-like electronic structure (**7b**) will show a hypsochromic shift for the same solvent change (negative solvatochromism).⁴³

The consequences of such a change in electronic structure on the position of absorption have been calculated on the basis of valence-bond theory by Forster in 1939.⁴³ According to his calculations, an intermediate meropolymethine (**7b**) with equal contributions from both mesomeric structures (**7a**) and (**7c**) will have the longest-wavelength absorption.

Quantitative calculations of the solvent dependence of UV-Vis absorption spectra based on different models have been carried out by a number of workers.⁴⁴⁻⁵⁹

Based on the direction of spectral shifts of the azo merocyanines in this study with increasing solvent polarity, it is inferred that μ_g is lower than μ_e for all the solutes examined. This suggests that as the solute dipole moment increases during the electronic transition, the Franck-Condon excited state is more solvated by dipole-solvent polarisation, causing a red shift (bathochromic). This implies that increasing solvent polarity shifts the electronic structure from a polyene-like state (**7a**) to a more polymethine-like state (**7b**).

Focusing our attention on the second feature, namely the influence of the azo moiety, we compare dye **1** with the iso-electronic methine dye **8**. Solvent effects have been known to depend largely on differing dipolar characteristics of a molecule when it is promoted to the excited state. Depending on the change in the dipolar characteristics between the ground and excited states, three possibilities exist, as shown in Table 2.

In view of the above discussion, and also from the theoretical work on dye **8** by Benson & Murrell,⁶¹ it is inferred that **8** can be classified as a moderately dipolar dye in relatively non-polar solvents, whereas in strongly polar media it is regarded as a highly dipolar dye. The reverse

TABLE 2
Summary of the Properties of the Three Main Types of Merocyanine Dyes^{60,64}

Type	Ground state		Excited state		Solvent-induced shift
	Polarity	Bond length alternation	Polarity	Bond length alternation	
Weakly dipolar	Low	High	Increased	Reduced	Bathochromic
Moderately dipolar	Medium	Low	Little change	Little change	
Highly dipolar	High	High	Reduced	Reduced	Hypsochromic

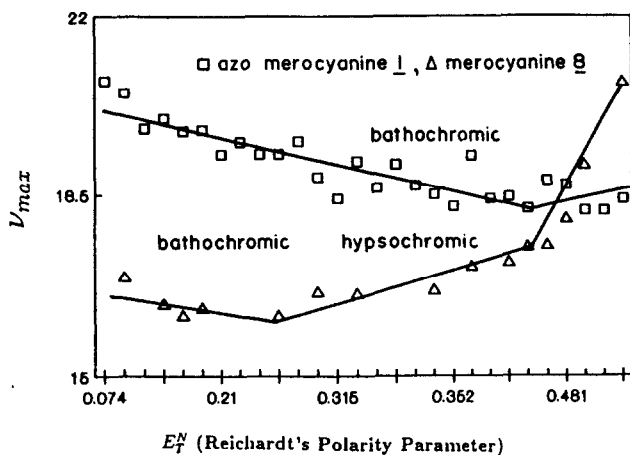


Fig. 5. Plot showing the reverse solvatochromism in **1** and **8** at different regions of solvent polarity.

solvatochromism arises from a possible change in the electronic configuration, i.e. from the quinoidal form to the benzenoid structure. Botrel *et al.* have shown that the calculated dipole moments exhibit the following evolution: $\mu_g < \mu_e$ in less polar solvents, and $\mu_g > \mu_e$ in highly polar solvents.⁶²

The effect of structural change on replacement of the $-\text{CH}=\text{CH}-$ bridge by $-\text{N}=\text{N}-$ is seen through comparison of the plots of spectral data for **8** and **1** vs the E_T^N parameters.^{9,10} The trends observed are shown in Fig. 5, from which the following is apparent:

- The merocyanine dye **8** exhibits a *bathochromic* shift in non-polar solvents ($E_T^N = 0.0-0.26$). This suggests that **8** is a weakly dipolar dye.
- Dye **8** reverses its solvatochromic property in the region of higher solvent polarity ($E_T^N \geq 0.26$) and displays a *hypsochromic* shift, characteristic of a highly dipolar dye.
- In contrast, the azo merocyanine **1** exhibits a *bathochromic* shift in the solvent polarity region $E_T^N = 0.0-0.41$; this is characteristic of a weakly dipolar dye.
- Dye **1** displays a slight reversal in its solvatochromic behaviour in the region $E_T^N = 0.41-0.80$, characteristic of a moderately dipolar dye.

Figure 5 shows the complete range of spectral response of merocyanine dyes, as the $-\text{C}=\text{C}-$ linkage is replaced by the $-\text{N}=\text{N}-$ moiety, i.e.

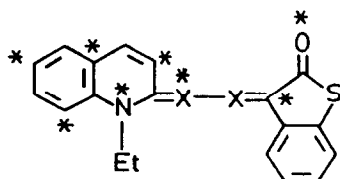
Weakly dipolar \rightarrow moderately dipolar (azo merocyanine, **1**)

Weakly dipolar \rightarrow moderately dipolar \rightarrow highly dipolar (merocyanine, **8**)

The azo merocyanine **1** is not a highly dipolar dye; rather it is a weakly

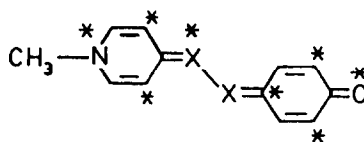
dipolar dye in the region $E_T^N = 0.0-0.6$, slowly tending towards moderately dipolar in more polar solvents with $E_T^N \geq 0.6$. Hence it does not show strongly hypsochromic shifts as would have been expected. A similar trend is observed for dyes 2-6.

Secondly, from Fig. 5, it is seen that **1** absorbs at shorter wavelengths than does its carbon analogue **8**. Such a trend has been reported earlier by Glauert & Mann for dye **9** $X = CH$, λ_{\max}^{MeOH} 554 nm; $X = N$, λ_{\max}^{EtOH} 454 nm.⁶³



9a, $X = CH$

9b, $X = N$



10a, $X = CH(8)$

10b, $X = N(1)$

This kind of behaviour has been rationalised using perturbational theory.⁶⁰ According to Dewar's rules, an electronegative hetero-atom or an electron-withdrawing group placed at the central starred atom in **9** should give a hypsochromic shift. This reasoning can be extended to **1**. However, the opposing spectral effects at the conjugating bridge containing the $-N=N-$ group at the starred and unstarred positions are not equal. This could possibly lead to hypsochromic shifts compared with its carbon analogue. This hypsochromic shift resulting from the structural change **9a** \rightarrow **9b**, or **10a** \rightarrow **10b**, should not be confused with the hypsochromic shift arising from varying solvent polarity.

Thirdly, it is seen that the extent of shifts for **8** is considerably larger than for **1**.

Our final objective was achieved by treating the spectral data in an iterative fashion to obtain a new polarity scale, the π_{azo}^* scale.¹⁷ The π_{azo}^* scale has been evaluated against several polarity scales and various solvatochromic dyes. The analysis can be found in our earlier reports.^{17,18}

4 CONCLUSIONS

The azo merocyanine dyes synthesised for this study displayed strong solvatochromic characteristics. The electronic spectral evaluation of these dyes strongly suggests that with increasing solvent polarity, μ_g becomes lower than μ_e , implying a shift in electronic structure, i.e. from a polyene-like structure to more polymethine like structure. The spectral data obtained were also used to formulate a new solvent polarity scale, the π_{azo}^* scale.

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