



## Phenyl 3-Aminobenzenesulphonates: New Intermediates for Arylazopyridone Disperse Dyes†

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### ABSTRACT

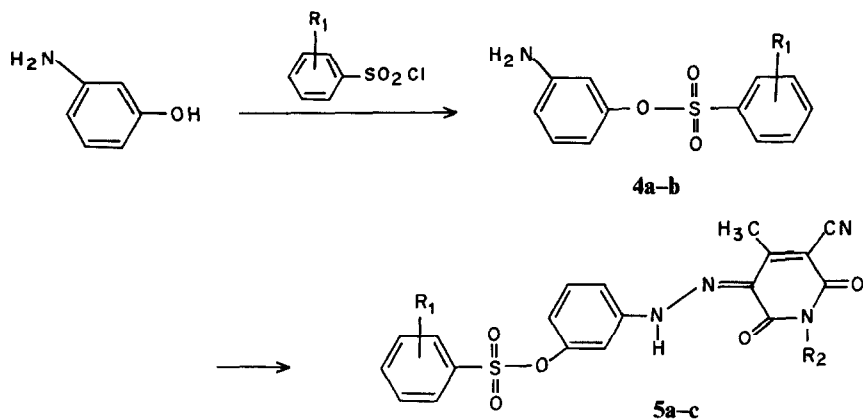
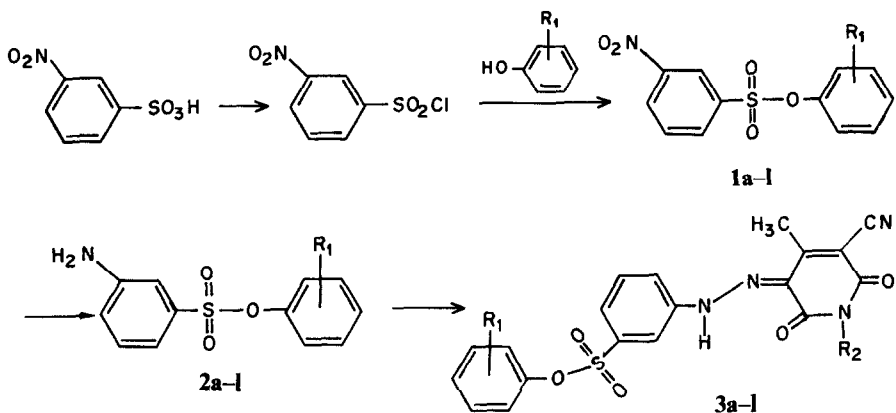
*Several newer disperse dyes 3a–3l have been synthesized from phenyl 3-aminobenzenesulphonates as diazo-components. Their coloristic and dyeing properties have been evaluated, and their performance compared with corresponding dyes 5 derived from 3-aminophenyl phenylsulphonates 4. The new dyes 3 possess good fastness and dyeing properties. Moreover, they have higher tinctorial strength as compared with the dyes 5, which include the commercial dye Samaron Yellow 6 GRL (5b), making them highly competitive commercially.*

### 1 INTRODUCTION

Several monoazo disperse dyes derived from pyridones as coupling components have been synthesized and extensively studied for their usefulness as fast yellow dyes on polyester fibres.<sup>1,2</sup> The more recent patent literature has described yellow pyridone disperse dyes derived from 3-aminophenyl phenylsulphonates (4) as diazo-components.<sup>3,4</sup> However, we can find no data on pyridine yellows derived from phenyl 3-aminobenzenesulphonates (2) (Scheme 1) as diazo-components. The intermediate 2 would give rise to newer dyes 3 (Scheme 1) in which the —O—SO<sub>2</sub>— linkage is reversed with respect to the azo chromophore *vis à vis* the patented dyes 5

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(Scheme 2) derived from **4**. It was thought that this reversal, leading to an alteration in the  $\pi$ -electron distribution of the chromophoric system, could afford better dyes. This communication reports the synthesis of several newer disperse dyes **3** derived from the diazo-component **2** (Scheme 1). Their coloristic and dyeing properties have been evaluated. The performance of the dyes **3** is also compared with the corresponding dyes **5** derived from **4**.

## 2 EXPERIMENTAL

### 2.1 General

Melting points recorded are uncorrected. The UV-visible spectra were recorded on a Perkin-Elmer 350 spectrophotometer, IR spectra on a

Perkin–Elmer 137B spectrophotometer and the  $^1\text{H}$ -NMR spectra were run on Varian T-60 and Bruker WH-90 FT spectrometers in trifluoroacetic acid containing 0.1% TMS as internal standard. The chemical shifts are expressed in  $\delta$  ppm. Mass spectra were recorded on a CEC 21-110B or Finnigan MAT-1020 automated GC/MS mass spectrometer at minimum source temperature.

## 2.2 Preparation of phenyl 3-nitrobenzenesulphonates (1)

### 2.2.1 General procedure

To a vigorously stirred mixture of phenol (0.08 mol), potassium carbonate (3 g) and tetrabutylammonium bromide (2.5 g) in a mixture of 5% sodium hydroxide solution (100 ml) and benzene (250 ml), *m*-nitrobenzene sulphonyl chloride (17.05 g, 0.08 mol) was added dropwise over 2 h. The mixture was stirred for a further 6 h at 30°C. The benzene layer was removed and the aqueous layer was extracted twice with benzene (50 ml). The combined benzene extract was distilled under reduced pressure to remove the solvent. Recrystallization of the residue from benzene afforded pure **1**. The melting points yields and elemental analyses of **1** are as follows.

*Phenyl 3-nitrobenzenesulphonate, 1a*. White needles from benzene: m.p. 90°C; yield, 96%. Calculated for  $\text{C}_{12}\text{H}_9\text{NO}_5\text{S}$ : C, 51.6; H, 3.2; N, 5.0. Found: C, 51.4; H, 3.1; N, 4.9%.

*p*-Chlorophenyl 3-nitrobenzenesulphonate, **1b**. White needles from benzene: m.p. 105°C; yield 86%. Calculated for  $\text{C}_{12}\text{H}_8\text{ClNO}_5\text{S}$ : C, 45.9, H, 2.6; N, 4.5. Found: C, 45.7; H, 2.4; N, 4.3%.

*m*-Cresyl 3-nitrobenzenesulphonate, **1c**. White needles from benzene: m.p. 76°C; yield 90%. Calculated for  $\text{C}_{13}\text{H}_{11}\text{NO}_5\text{S}$ : C, 55.2; H, 3.7; N, 4.8. Found: C, 55.1; H, 3.6; N, 4.8%.

*o*-Cresyl 3-nitrobenzenesulphonate, **1d**. White needles from benzene: m.p. 58°C; yield 93%. Calculated for  $\text{C}_{13}\text{H}_{11}\text{NO}_5\text{S}$ : C, 53.2; H, 3.7; N, 4.8. Found: C, 53.0; H, 3.5; N, 4.6%.

## 2.3 Preparation of phenyl 3-aminobenzenesulphonates 2

### 2.3.1 General procedure

A mixture of **1** (0.06 mol), stannous chloride dihydrate (55 g) and concentrated hydrochloric acid (60 ml) was refluxed for 6 h. The mixture was cooled and made basic with sodium hydroxide solution to afford the crude

product. Recrystallization from benzene gave pure **2** in excellent yields. The melting points, yields and elemental analyses of **2** are as follows.

*Phenyl 3-aminobenzenesulphonate, 2a.* M.p. 78°C; yield, 90%. Calculated for  $C_{12}H_{11}NO_3S$ : C, 57.8; H, 4.4; N, 5.6. Found: C, 57.6; H, 4.1; N, 5.5%.

*p-Chlorophenyl 3-aminobenzenesulphonate, 2b.* M.p. 85°C; yield, 95%. Calculated for  $C_{12}H_{10}ClNO_3S$ : C, 50.9; H, 3.5; N, 4.9. Found: C, 50.7; H, 3.4; N, 4.7%.

*m-Cresyl 3-aminobenzenesulphonate, 2c.* M.p. 63°C; yield, 90%. Calculated for  $C_{13}H_{13}NO_3S$ : C, 59.3; H, 4.9; N, 5.3. Found: C, 59.1; H, 4.7; N, 5.2%.

*o-Cresyl 3-aminobenzenesulphonate, 2d.* M.p. 108°C; yield, 89%. Calculated for  $C_{13}H_{13}NO_3S$ : C, 59.3; H, 4.9; N, 5.3. Found: C, 59.2; H, 4.7; N, 5.1%.

## 2.4 Preparation of disperse dyes 3

### 2.4.1 General procedure

A solution of an *N*-substituted 3-cyano-6-hydroxy-4-methyl pyrid-2(1*H*)-one (0.01 mol) in aqueous sodium hydroxide (10%, w/v; 5 ml) was cooled to 5°C. A diazo solution of **2** [prepared by diazotizing a solution of **2** (0.01 mol) in 1:1 aqueous hydrochloric acid (6 ml) with sodium nitrite (0.01 mol) in water (5 ml)] was added with constant stirring. The product was filtered, washed with water, dried and recrystallized from benzene to yield the yellow dyes **3**. The structures of **3** were in accord with their IR,  $^1H$ -NMR and mass spectral analyses. Substituents, melting points, yields and elemental analyses of **3** are as follows

**3a:**  $R_1 = H$ ,  $R_2 = CH_3$ ; m.p. 205°C; yield, 90%. Calculated for  $C_{20}H_{16}N_4O_5S$ : C, 56.6; H, 3.8; N, 13.2. Found: C, 56.5; H, 3.5; N, 13.0%.

**3b:**  $R_1 = H$ ,  $R_2 = C_2H_5$ ; m.p. 182°C; yield, 60%. Calculated for  $C_{21}H_{18}N_4O_5S$ : C, 57.5; H, 4.1; N, 12.8. Found: C, 57.2; H, 4.0; N, 12.5%.

**3c:**  $R_1 = H$ ,  $R_2 = C_6H_5$ ; m.p. 230°C; yield, 60%. Calculated for  $C_{25}H_{18}N_4O_5S$ : C, 61.7; H, 3.7; N, 11.5. Found: C, 61.5; H, 3.5; N, 11.4%.

**3d:**  $R_1 = p\text{-Cl}$ ,  $R_2 = CH_3$ ; m.p. 170°C; yield, 63%. Calculated for  $C_{20}H_{15}ClN_4O_5S$ : C, 52.3; H, 3.3; N, 12.2. Found: C, 52.1; H, 3.0; N, 12.0%.

**3e:**  $R_1 = p\text{-Cl}$ ,  $R_2 = \text{C}_2\text{H}_5$ ; m.p.  $190^\circ\text{C}$ ; yield, 60%. Calculated for  $\text{C}_{21}\text{H}_{17}\text{ClN}_4\text{O}_5\text{S}$ : C, 53.3; H, 3.6; N, 11.8. Found: C, 53.1; H, 3.5; N, 11.6%.

**3f:**  $R_1 = p\text{-Cl}$ ,  $R_2 = \text{C}_6\text{H}_5$ ; m.p.  $150^\circ\text{C}$ ; yield, 60%. Calculated for  $\text{C}_{25}\text{H}_{17}\text{ClN}_4\text{O}_5\text{S}$ : C, 57.6; H, 3.3; N, 10.8. Found: C, 57.5; H, 3.2; N, 10.7%.

**3g:**  $R_1 = m\text{-CH}_3$ ,  $R_2 = \text{CH}_3$ ; m.p.  $113^\circ\text{C}$ ; yield, 80%. Calculated for  $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_5\text{S}$ : C, 57.5; H, 4.1; N, 12.8. Found: C, 57.2; H, 4.0; N, 12.5%.

**3h:**  $R_1 = m\text{-CH}_3$ ,  $R_2 = \text{C}_2\text{H}_5$ ; m.p.  $170^\circ\text{C}$ ; yield, 76%. Calculated for  $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_5\text{S}$ : C, 58.4; H, 4.4; N, 12.4. Found: C, 58.1; H, 4.2; N, 12.1%.

**3i:**  $R_1 = m\text{-CH}_3$ ,  $R_2 = \text{C}_6\text{H}_5$ ; m.p.  $260^\circ\text{C}$  (dec.); yield, 60%. Calculated for  $\text{C}_{26}\text{H}_{20}\text{N}_4\text{O}_5\text{S}$ : C, 62.4; H, 4.0; N, 11.2. Found: C, 62.2; H, 3.9; N, 11.0%.

**3j:**  $R_1 = o\text{-CH}_3$ ,  $R_2 = \text{CH}_3$ ; m.p.  $178^\circ\text{C}$ ; yield, 90%. Calculated for  $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_5\text{S}$ : C, 57.5; H, 4.1; N, 12.8. Found: C, 57.4; H, 4.0; N, 12.6%.

**3k:**  $R_1 = o\text{-CH}_3$ ,  $R_2 = \text{C}_2\text{H}_5$ ; m.p.  $169^\circ\text{C}$ ; yield, 78%. Calculated for  $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_5\text{S}$ : C, 55.7; H, 4.4; N, 12.3. Found: C, 55.6; H, 4.3; N, 12.1%.

**3l:**  $R_1 = o\text{-CH}_3$ ,  $R_2 = \text{C}_6\text{H}_5$ ; m.p.  $250^\circ\text{C}$ ; yield, 60%. Calculated for  $\text{C}_{26}\text{H}_{20}\text{N}_4\text{O}_5\text{S}$ : C, 62.4; H, 4.0; N, 11.2. Found: C, 62.1; H, 3.9; N, 11.0%.

## 2.5 Preparation of 3-aminophenyl phenylsulphonates 4

The compounds **4a** and **4b** were prepared exactly as described in the general procedure in Section 2.2, employing *m*-aminophenol and arylsulphonyl chloride as the reactants. The substituents, melting points, yields and elemental analyses are as follows.

**4a:**  $R_1 = \text{H}$ , m.p.  $95^\circ\text{C}$ ; yield, 90%. Calculated for  $\text{C}_{12}\text{H}_{11}\text{NO}_3\text{S}$ : C, 57.8; H, 4.4; N, 5.6. Found: C, 57.7; H, 4.3; N, 5.6%.

**4b:**  $R_1 = m\text{-CH}_3$ ; m.p.  $93^\circ\text{C}$ ; yield, 80%. Calculated for  $\text{C}_{13}\text{H}_{13}\text{NO}_3\text{S}$ : C, 59.3; H, 4.9; N, 5.3. Found: C, 59.0; H, 4.8; N, 5.1%.

## 2.6 Preparation of dyes 5a–5c

### 2.6.1 General procedure

A solution of the *N*-substituted 3-cyano-5-hydroxy-4-methyl-pyrid-2(1*H*)-one (0.01 mol) in aqueous sodium hydroxide (10% w/v; 5 ml) was cooled to  $5^\circ\text{C}$ . A diazo solution of **4** [prepared by diazotizing a solution of **4a** or **4b** (0.01 mol) in 1:1 hydrochloric acid (6 ml) with sodium nitrite (0.01 mol) in water (5 ml)] was added with constant stirring to the above solution. The separated crude product was filtered, washed with water, dried and

recrystallized from benzene. The structures of the dyes **5a–5c** were in accord with their IR,  $^1\text{H-NMR}$  mass spectral analyses. The substituents, melting points, yields and elemental analyses of **5a–5c** are as follows.

**5a:**  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{CH}_3$ ; m.p.  $208^\circ\text{C}$ ; yield, 80%. Calculated for  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_5\text{S}$ : C, 56.6; H, 3.8; N, 13.2. Found: C, 56.5; H, 3.8; N, 13.1%.

**5b:**  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{C}_2\text{H}_5$ ; m.p.  $250^\circ\text{C}$ ; yield, 86%. Calculated for  $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_5\text{S}$ : C, 57.6; H, 4.1; N, 12.8. Found: C, 57.4; H, 3.9; N, 12.5%.

**5c:**  $\text{R}_1 = m\text{-CH}_3$ ,  $\text{R}_2 = \text{C}_2\text{H}_5$ ; m.p.  $188^\circ\text{C}$ ; yield, 90%. Calculated for  $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_5\text{S}$ : C, 58.4; H, 4.4; N, 12.4. Found: C, 58.3; H, 4.3; N, 12.1%.

### 3 RESULTS AND DISCUSSION

The intermediate phenyl 3-aminobenzenesulphonates **2a–2l** were prepared from the readily available *m*-nitrobenzenesulphonic acid (Scheme 1). *m*-Nitrobenzenesulphonic acid was initially converted to *m*-nitrobenzenesulphonyl chloride by a reported procedure,<sup>5</sup> and the sulphonyl chloride was then reacted with substituted phenols at ambient temperatures under alkaline conditions in a biphasic system using tetrabutylammonium bromide as phase transfer catalyst (PTC). The reaction afforded the nitrosulphonic esters (**1a–1l**) in excellent yields (90–96%). Subsequent reduction of **1** with stannous chloride and concentrated hydrochloric acid gave **2**, the structures of which were confirmed by spectral and elemental analyses. Diazotization of **2** followed by coupling with substituted pyridones yielded the dyes **3**, which have bright greenish yellow to golden yellow hues. The IR spectra of the dyes **3a–3l** in nujol showed characteristic frequencies at  $2260\text{ cm}^{-1}$  due to a nitrile function and at  $1640\text{ cm}^{-1}$  due to a carbonyl group. Their  $^1\text{H-NMR}$  spectra in trifluoroacetic acid confirmed the structures. The mass spectra of all the dyes **3** revealed the molecular ion peaks with good relative abundance.

Alternatively, the dyes **5** were obtained by the route shown in Scheme 2. The reaction of *m*-aminophenol with the corresponding substituted benzenesulphonyl chlorides in the presence of tetrabutylammonium chloride as PTC afforded the 3-aminophenyl benzenesulphonates **4** in excellent yields (85–90%). The corresponding dye **5** was synthesized from **4** by the usual diazotization and coupling reactions.

#### 3.1 Visible spectral characteristics

The visible spectral characteristics of the dyes **3** and **5** are summarized in Table 1. Absorption maxima (415–422 nm) of dyes **3** closely resemble

**TABLE 1**  
Visible Spectral Characteristics and Fastness Properties (on Polyester) of **3** and **5**

Dye	$R_1$	$R_2$	$\lambda_{\max}$ (nm)	$\epsilon$ ( $\text{mol}^{-1} \text{cm}^{-1}$ )	Light fastness	Sublimation fastness
<b>3a</b>	H	CH <sub>3</sub>	422	34 000	6	4
<b>3b</b>	H	C <sub>2</sub> H <sub>5</sub>	422	34 770	6	4
<b>3c</b>	H	C <sub>6</sub> H <sub>5</sub>	418	25 820	4–5	5
<b>3d</b>	<i>p</i> -Cl	CH <sub>3</sub>	420	24 360	5	5
<b>3e</b>	<i>p</i> -Cl	C <sub>2</sub> H <sub>5</sub>	420	30 660	5–6	4–5
<b>3f</b>	<i>p</i> -Cl	C <sub>6</sub> H <sub>5</sub>	420	29 200	5	4–5
<b>3g</b>	<i>m</i> -CH <sub>3</sub>	CH <sub>3</sub>	420	29 380	6	4–5
<b>3h</b>	<i>m</i> -CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	420	31 300	5–6	4–5
<b>3i</b>	<i>m</i> -CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	420	27 000	3–4	4–5
<b>3j</b>	<i>o</i> -CH <sub>3</sub>	CH <sub>3</sub>	415	35 030	5–6	4–5
<b>3k</b>	<i>o</i> -CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	421	38 330	6	4
<b>3l</b>	<i>o</i> -CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	420	24 690	3–4	4–5
<b>5a</b>	H	CH <sub>3</sub>	423	15 100	5	4
<b>5b</b>	H	C <sub>2</sub> H <sub>5</sub>	422	23 270	5–6	4
<b>5c</b>	<i>m</i> -CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	423	28 070	5	4

those of the dyes **5**. However, a study of molar extinction coefficients ( $\epsilon$  values) of the dyes **3** and **5** led to more interesting conclusions. The newer dyes **3** derived from phenyl 3-aminobenzenesulphonates had much higher  $\epsilon$  values giving brighter yellows in comparison to the dyes **5** derived from 3-aminophenyl benzenesulphonates. Typically, dye **3a** had a molar extinction coefficient nearly twice that of **5a**. Among the new dyes **3**, the dyes derived from *N*-alkylpyridones have higher tinctorial strength than the dyes derived from *N*-phenylpyridones. Moreover, the substituents present in the diazocomponent **2** have brought about variations in the molar extinction coefficients of the dyes **3**. Thus, the  $\epsilon$  values for the dyes which carry a methyl substituent in the *o*-position (**3j** and **3k**) are greater than those obtained for *m*-methyl (**3g** and **3h**) and *p*-chloro (**3d** and **3e**) substituents.

### 3.2 Dyeing characteristics

The dyes were applied on polyester by a high-pressure high-temperature dyeing technique. Lightfastness was determined by exposing the dyed polyester on an Atlas Fadometer for 24 h; the fading was assessed by the following ratings using standard procedures: 1, poor; 3, moderate; 5, good; 6, excellent. For sublimation fastness determinations, the dyed polyester fibre was stitched between two pieces of undyed polyester fibres [stain cloth] of equal lengths. This system was subjected to 200°C for 1 min. Any staining on

the undyed piece, change in tone or loss in depth were assessed on a 1 (poor) to 5 (very good) rating.

The dyes **3** coloured polyester fibre in bright greenish yellow shades showing excellent build-up to deep shades, in all cases better than that of the dyes **5**. In particular, the dyes **3a**, **3b**, **3j** and **3k** gave bright yellow dyeings with greenish yellow hues of good clarity.

Lightfastness of the majority of the dyes was good, dyes **3a**, **3b**, **3g** and **3k** in particular showing excellent fastness. The lighter dyeings obtained with the dyes **3i** and **3l** from *N*-phenylpyridones had moderate lightfastness. No significant variation in the sublimation fastness properties of the dyes **3** and **5** was observed. In general, sublimation fastness ranged from good to very good for all the dyes.

#### 4 CONCLUSION

The dyes **3** derived from phenyl 3-aminobenzenesulphonates **2** and *N*-alkylpyridones possess good fastness and dyeing properties. In addition, they have higher molar extinction coefficients, and consequently, higher tinctorial strength than the commercial pyridone yellows such as Samaron Yellow 6GRL (**5b**) derived from 3-aminophenyl phenylsulphonates.

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