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The Use of *ortho*-Cumidine as a Dyestuff Intermediate. Part 1: Monoazo and Disazo Solvent Dyes*

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SUMMARY

A potential industrial outlet for o-cumidine as an intermediate for new monoazo and disazo solvent dyes is reported. New solvent dyes prepared from o-cumidine had much better solubilities than the corresponding commercial dyes derived from o-toluidine. Absorption maxima of the o-cumidine-based dyes were generally comparable with those of analogous o-toluidine derivatives, although a large difference was apparent in one disazo system studied. Although the monoazo dyes showed somewhat lower tinctorial strength, the disazo dyes exhibited better tinctorial power. The performance of 4-o-cumylazo-o-cumidine as a Fast Base was comparable with that of Fast Garnet GBC Base.

1 INTRODUCTION

The *para* isomer of cumidine is an important intermediate and finds extensive use in the manufacture of herbicides such as isoproturon. The industrial process for the manufacture of *p*-cumidine involves[1] the mixed acid nitration of cumene, then fractionation of the resulting mixed nitrocumenes to isolate *p*-nitrocumene, followed by reduction. Alternatively, the nitration mixture is reduced to give mixed cumidines from which the individual isomers are isolated taking advantage of the differences in their pK_B values. The economy of the process would be improved if industrial outlets for *o*-cumidine could be found. In this present

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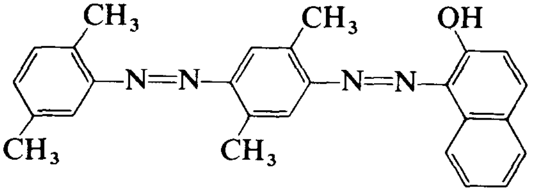
communication, we have studied the use of *o*-cumidine as an intermediate for azo solvent dyes.

Out of the total number of 346 solvent azo dyes recorded in the *Colour index*,[2] only 82 have the chemical constitution disclosed. Of these, there are six solvent dyes based on *o*-toluidine as diazo component which have been commercialised (Schemes 1 and 2). In this paper, we have compared the solvent dye characteristics of these six commercial solvent dyes with those of the corresponding new mono- and dis-azo dyes derived from *o*-cumidine as diazo component.

The structure of Waxoline Red OS (**1**) was investigated and shown to be a disazo dye derived from 2,5-xylidine. It was found to have better solubility than the corresponding disazo dye derived from *o*-toluidine, Waxoline Red O (**4a**).[3] This improved solubility of **1** could be attributable to the additional methyl group present in the diazo component of the dye. It was thus felt that solvent dyes derived from *o*-cumidine, having an enhanced and bulkier alkyl chain, would also show improved properties.



1

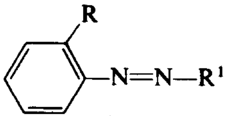
2 RESULTS AND DISCUSSION

2.1 Synthesis of *o*-cumidine

The nitration of cumene[1] yielded *p*-nitrocumene 63·6%, *m*-nitrocumene 6·4%, and *o*-nitrocumene 25·2% as indicated by GLC analysis. *o*-Nitrocumene was separated by fractional distillation under reduced pressure using 'Hyflux' column packings. The *o*-nitrocumene distilled over at 110°C/10 mm and was assayed to be 99·8% pure by GLC. The reduction of *o*-nitrocumene to *o*-cumidine was carried out by iron and hydrochloric acid.[4]

2.2 Monoazo solvent dyes

o-Cumidine was diazotised and coupled with 2-naphthol, 1-naphthol, and *p*-cresol to give the new monoazo dyes **2b**, **2d** and **2f** (Scheme 1). The properties of the new dyes were compared with those of the corresponding commercial dyes **2a**, **2c** and **2e**.



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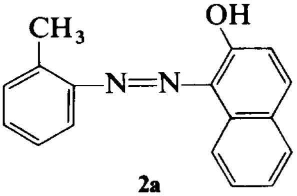
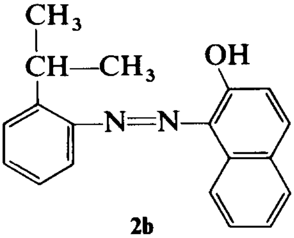
Dye	*R*	*Coupling component for R^1*	*Name*
2a	CH_3	2-Naphthol	Solvent Orange 2
2b	$CH(CH_3)_2$	2-Naphthol	
2c	CH_3	1-Naphthol	Solvent Red 2
2d	$CH(CH_3)_2$	1-Naphthol	
2e	CH_3	*p*-Cresol	Solvent Yellow 12
2f	$CH(CH_3)_2$	*p*-Cresol	

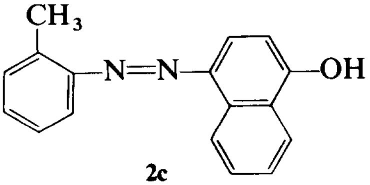
Scheme 1



2a



2b



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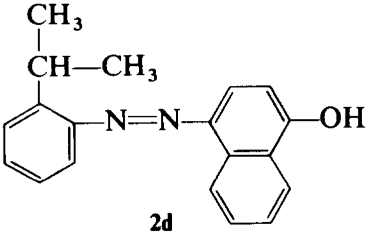

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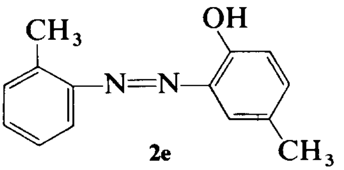
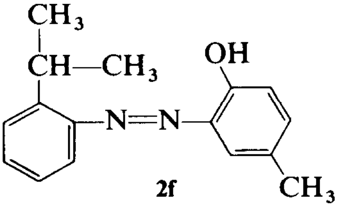


2e



2f

2.2.1. *Solubility studies*

The solubilities of the purified dyes in different solvents were evaluated (see the Experimental section) and are recorded in Tables 1, 2 and 3. The new dye **2b**, depending on the solvent, was about 5–135% more soluble in polar solvents and 15–182% more soluble in non-polar solvents compared with Solvent Orange 2 (**2a**). Similarly, the dye **2d** was 17–300% more soluble than

TABLE 1
Comparison of Solubility Data of Dyes **2a** and **2b**

Solvent	*Solubility (g/100 g solvent)*			*Percentage increase*
	*Solvent Orange 2 (**2a**)*		*Dye **2b***	
	Reported[5]	*Found*		
Ethanol	1·00	0·89	1·30	46
Acetone	2·80	2·60	2·83	9
Stearic acid	2·40	3·00	4·66	53
Cellosolve	—	1·01	2·38	135
Ethyl acetate	2·00	2·30	3·63	59
Butyl acetate	3·00	3·10	3·33	7
Methanol	—	0·19	0·18	5
Toluene	4·00	5·00	12·50	150
p-Xylene	—	9·00	9·00	—
Kerosene	—	1·08	1·80	66
Paraffin wax	0·60	0·70	1·98	182
Carbon tetrachloride	—	4·76	5·50	15
Benzene	2·80	3·00	6·00	50

TABLE 2
Comparison of Solubility Data of Dyes **2c** and **2d**

Solvent	*Solubility (g/100 g solvent)*		*Percentage increase*
	*Solvent Red 2 (**2c**)*	*Dye **2d***	
Ethanol	4·80	6·30	31
Acetone	12·30	15·90	29
Stearic acid	10·30	20·80	101
Cellosolve	12·50	25·00	100
Ethyl acetate	10·80	18·30	69
Butyl acetate	12·50	25·00	100
Methanol	12·80	20·30	58
Toluene	20·00	26·40	32
p-Xylene	25·80	31·30	17
Kerosene	1·20	4·80	300
Paraffin wax	8·20	15·07	83
Carbon tetrachloride	8·20	10·30	23
Benzene	15·00	20·00	33

TABLE 3
Comparison of Solubility Data of Dyes **2e** and **2f**

Solvent	*Solubility (g/100 g solvent)*		*Percentage increase*
	Solvent Yellow 12 (2e)	*Dye 2f*	
Ethanol	12·80	15·70	22
Acetone	10·30	12·80	24
Stearic acid	12·70	18·30	44
Cellosolve	2·20	2·80	27
Ethyl acetate	10·80	18·70	73
Butyl acetate	11·00	20·00	81
Methanol	8·70	18·30	110
Toluene	18·30	28·40	55
p-Xylene	20·90	35·00	67
Kerosene	3·30	10·00	203
Paraffin wax	6·80	7·30	7
Carbon tetrachloride	8·20	12·70	54
Benzene	15·80	25·30	60

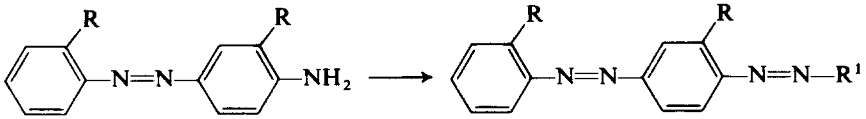
Solvent Red 2. The percentage increase in solubilities ranged from 7–203 for the dye **2f** compared with the commercial Solvent Yellow 12.

2.2.2. *Ultraviolet–visible spectra of* **2**

The electronic spectra of dyes **2a**–**2f** were recorded in chloroform and the results are summarised in Table 4. The dyes **2b** and **2d** showed absorption maxima comparable with those of the corresponding commercial dyes **2a** and **2c**. The dye **2f**, however, showed a bathochromic shift ranging from 37 to 60 nm. All the new monoazo dyes derived from *o*-cumidine had lower tinctorial strength compared with the commercial dyes.

TABLE 4
Visible Spectral Data of Monoazo Dyes **2** and **3**

Dye	λ_{max} *(nm)*	*log* ε	λ_{max} *(nm)*	*log* ε
2a	490	4·36	510	4·33
2b	492	4·23	520	4·18
2c	413	4·13	462	4·80
2d	398	4·05	460	3·76
2e	335	4·33	383	4·00
2f	390	4·28	420	3·73
3a	376	4·61	—	—
3b	375	4·68	—	—



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4 or 5

Dye	*R*	*Coupling component, R^1*	*Name*
3a	CH_3	—	
3b	$CH(CH_3)_2$	—	
4a	CH_3	2-Naphthol	Solvent Red 24
4b	$CH(CH_3)_2$	2-Naphthol	
4c	CH_3	Phenol	Solvent Orange 13
4d	$CH(CH_3)_2$	Phenol	
4e	CH_3	3-Methyl-5-pyrazolone	
4f	$CH(CH_3)_2$	3-Methyl-5-pyrazolone	
5a	CH_3	Naphthol AS	
5b	$CH(CH_3)_2$	Naphthol AS	
5c	CH_3	Naphthol ASD	
5d	$CH(CH_3)_2$	Naphthol ASD	
5e	CH_3	Naphthol ASE	
5f	$CH(CH_3)_2$	Naphthol ASE	
5g	CH_3	Naphthol ASTR	
5h	$CH\ (CH_3)_2$	Naphthol ASTR	

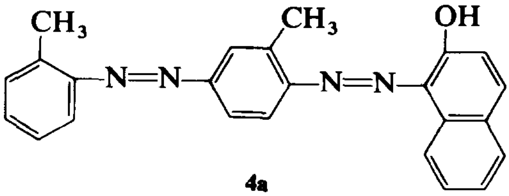
Scheme 2

*2.2.3 4-o-Cumylazo-o-cumidine (**3b**)*

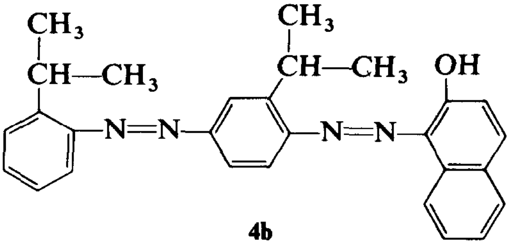
o-Cumidine was diazotised and self-coupled to give the aminoazo derivative, which rearranged in presence of small amounts of hydrochloric acid to give **3b** (Scheme 2). The corresponding *o*-toluidine dye (**3a**) is commercialised as Solvent Yellow 3. The hydrochloride of **3a** is also used as an azoic diazo component, viz. Fast Garnet GBC Base (C.I. 37210). The performance of **3b** as a solvent dye was compared with that of Solvent Yellow 3 (**3a**). The solubility data are recorded in Table 5. The new dye **3b** had higher solubility than **3a** with the percentage increase ranging from 8 to 295 in both polar and non-polar solvents. The wavelength maxima and tinctorial strength of the dyes **3a** and **3b** were comparable (Table 4).

2.3 Disazo solvent dyes (4)

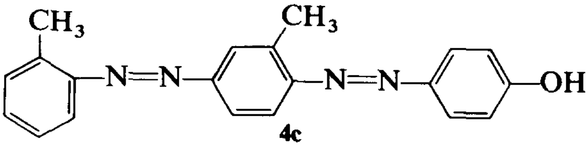
Disazo solvent dyes derived from Fast Garnet GBC Base (**3a**), such as Solvent Red 24 (**4a**) and Solvent Orange 13 (**4c**), are widely used as solvent dyes for the colouration of soaps, waxes, petroleum products, fats, oils, etc. The 4-*o*-cumylazo-*o*-cumidine (**3b**) was coupled with 2-naphthol and phenol



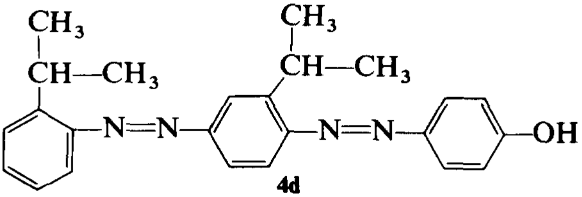
4a



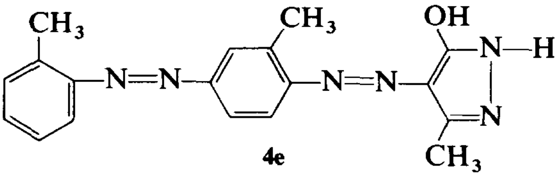
4b



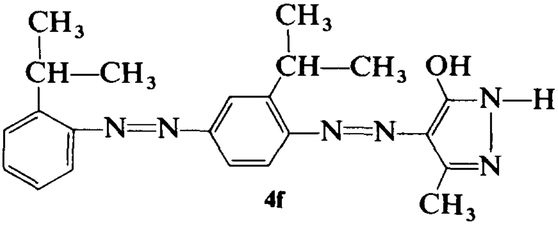
4c



4d



4e



4f

TABLE 5
Solubility Data of Dyes **3a** and **3b**

Solvent	*Solubility (g/100 g solvent)*[a]			*Percentage increase*
	*Solvent Yellow 3 (**3a**)*		*4-o-Cumylazo-o-cumidine (**3b**)*	
	Reported	*Found*		
Ethanol	5·0[b] 4·5[c]	4·23	5·12	21
Acetone	8·0[b] 25·00[c]	10·00	15·00	50
Stearic acid	8·00[c] 6·00[b]	7·00	11·50	60
Cellosolve	v.s.[b] 13·00[c]	14·00	18·00	28
Ethyl acetate	8·00[b] 20·00[c]	10·00	13·00	30
Butyl acetate	—	12·00	15·00	25
Methanol	6·00[c]	7·00	10·00	42
Toluene	3·60[b]	3·70	4·00	8
p-Xylene	4·6[b]	5·00	10·00	100
Kerosene	1·80[c]	0·70	1·60	128
Paraffin wax	0·50[b]	0·51	2·00	292
Carbon tetrachloride	—	4·43	6·43	45
Benzene	5·8[b]	5·70	12·00	110
Chloroform	—	30·00	40·00	33

[a] v.s., very soluble.
[b] Ref. 5.
[c] Ref. 6.

to give the red and orange dyes **4b** and **4d** (Scheme 2). The new dyes were purified by column chromatography on silica gel using petroleum ether/benzene as eluent. Their characteristics as dyes were compared with Solvent Red 24 and Solvent Orange 13. Similar coupling of **3b** with 3-methyl-5-pyrazolone gave the disazo dye **4f** which was compared with the dye **4e** derived from **3a.**

2.3.1 Solubility studies of disazo solvent dyes 4

The solubility data of the purified dyes **4a**, **4b** and **4c**, **4d** are recorded in Tables 6 and 7 respectively. Both the new dyes **4b** and **4d** derived from *o*-cumidine had much better solubilities in comparison with the corresponding commercial dyes **4a** and **4c** derived from *o*-toluidine. The percentage increase in solubility in the case of dye **4b** ranged from 27 to 645 (Table 6) in polar and non-polar solvents whereas in the case of dye **4d**, it ranged from 25 to 192 (Table 7a). Depending upon the solvent, the dye **4f** had much greater

TABLE 6

Comparison of Solubility Data of Dyes **4a** and **4b**

Solvent	*Solubility*[a] *(g/100 g solvent)*			*Percentage increase*
	*Solvent Red 24 (**4a**)*		*Dye **4b***	
	Reported	*Found*		
Ethanol	0·02–1[b] 0·2[c]	0·007	0·018	157
Acetone	0·15–3[b] 3·4[c]	0·070	0·490	64
Stearic acid	0·2–5[b] 3[c]	0·200	0·325	62
Cellosolve	s.s.[b] 0·7[c]	0·022	0·028	27
Ethyl acetate	2·5[c]	0·170	0·420	147
Butyl acetate	0·12–3[b]	0·140	0·590	320
Methanol	2[c]	0·003	0·006	100
Toluene	v.s.[b]	0·064	2·140	86
p-Xylene	—	0·800	1·720	115
Kerosene	0·8[c]	0·030	0·155	416
Paraffin wax	—	0·270	0·590	118
Carbon tetrachloride	—	0·400	2·980	645
Benzene	0·06–5[b]	1·720	4·560	165

[a] s.s., slightly soluble; v.s., very soluble.
[b] Ref. 5.
[c] Ref. 6.

solubilities, the percentage increase ranging from 43 to 1677 compared with the dye **4e** (Table 7b).

*2.3.2 Ultraviolet–visible spectra of the disazo dyes **4***

The UV–visible spectral data of the dyes **4** are recorded in Table 8. As compared with Solvent Red 24 (**4a**), the new dye **4b** showed a marginal bathochromic shift (3 nm) with better tinctorial strength. The new dye **4d** showed a considerable bathochromic shift (50 nm) with better tinctorial strength in comparison with Solvent Orange 13 (**4c**). The dyes **4e** and **4f** derived by using 3-methyl-5-pyrazolone had comparable wavelength maxima and tinctorial strength.

2.4 Evaluation of 4-*o*-cumylazo-*o*-cumidine (3b) as an azoic diazo component against Fast Garnet GBC base (3a)

Several disazo dyes **5** were synthesised from **3b** using various commercial naphthols as coupling components (Scheme 2). These new dyes were

TABLE 7a
Comparison of Solubility Data of Dyes **4c** and **4d**

Solvent	*Solubility (g/100 g solvent)*			*Percentage increase*
	*Solvent Orange 13 (**4c**)*		*Dye **4d***	
	Reported[5]	*Found*		
Ethanol	0·9	1·0	1·5	50
Acetone	2·8	2·7	3·5	30
Stearic acid	6·0	5·6	8·1	45
Cellosolve	—	2·0	4·1	105
Ethyl acetate	1·5	1·3	2·2	69
Butyl acetate	2·9	3·0	5·1	69
Methanol	—	0·6	1·1	83
Toluene	2·0	1·8	4·1	127
p-Xylene	—	3·0	6·2	107
Kerosene	1·0	0·8	1·2	50
Paraffin wax	2·0	1·8	3·1	72
Carbon tetrachloride	—	2·0	2·5	25
Benzene	1·5	1·4	4·1	192

TABLE 7b
Solubility Data of Dyes **4e** and **4f**

Solvent	*Solubility (g/100 g solvent)*		*Percentage increase*
	*Dye **4e***	*Dye **4f***	
Ethanol	0·160	0·23	43
Stearic acid	0·090	0·70	677
Butyl acetate	0·031	0·83	1 677
Kerosene	0·046	0·13	184
Paraffin wax	0·130	0·40	200
Chloroform	2·400	6·90	187

compared with the dyes derived from Fast Garnet GBC Base (**3a**) using the same series of naphthols (Scheme 2). The UV–visible spectra of the dyes (Table 8) showed comparable wavelength maxima and tinctorial strengths. The dyeing characteristics of the two series were also comparable.

3 EXPERIMENTAL

Melting points are uncorrected. Visible absorption spectra were recorded on a Beckman double-beam spectrophotometer Model 216 using chloroform

TABLE 8
Visible Spectra of Disazo Dyes **4** and **5**

Dye	λ_{max} *(nm)*	*log ε*
4a	520	4·25
4b	523	4·19
4c	475	4·13
4d	525	4·14
4e	450	4·69
4f	449	4·70
5a	543	4·54
5b	542	4·55
5c	537	4·56
5d	539	4·54
5e	545	4·64
5f	540	4·89
5g	540	4·49
5h	540	4·56

as solvent. Mass spectra were recorded on a CEC-21-110B double-focusing mass spectrometer using a direct inlet system at an ionisation voltage of 70 eV.

3.1 Synthesis of *o*-cumidine

The nitration of cumene was carried out following the procedure described by Haun and Kobe.[1] The separation of *o*-nitrocumene from the crude mixture was achieved by fractional distillation under reduced pressure 13 mm Hg) using a glass column of height 60 cm and i.d. 2·5 cm packed with 'Hyflux' stainless steel (s.s.) packings at a reflux ratio of 10:1. *o*-Nitrocumene of 99·5% purity (ascertained by GLC) distilled out at 110°C. It was then reduced using iron and hydrochloric acid.[4] At the end of the reduction, the reaction mixture was steam-distilled. The crude *o*-cumidine collected from the distillate was finally distilled under reduced pressure (13 mm Hg) to yield *o*-cumidine in 80% yield; b.p. 95°C/13 mm Hg.

3.2 Synthesis of 4-*o*-cumylazo-*o*-cumidine (3b)

o-Cumidine (13·5 g, 0·1 mol) was dissolved in a mixture of water (20 ml) and concentrated hydrochloric acid (6 ml, 0·5 mol). The solution was cooled to 0–5°C and a solution of sodium nitrite (3·45 g, 0·05 mol) in water (2 ml) was added dropwise with stirring at 0–5°C over 3–4 h. Sodium chloride (5 g) was added to the diazo solution portionwise, when a yellow precipitate separated. This was filtered, dried and suspended in a mixture of water (20 ml) and

TABLE 9

Properties and Analytical Data for Dyes Derived from *o*-Cumidine

Dye	*Recrystallisation solvent*	*Colour of crystals*	*M.p.* (°*C*)	*M*	*Required* (%)			*Found* (%)		
					C	*H*	*N*	*C*	*H*	*N*
2b	Benzene–pet. ether	Orange–red	140	290	78·6	6·2	9·7	78·5	6·1	9·6
2d	Benzene–pet. ether	Red	100	290	78·6	6·2	9·7	78·45	6·1	9·6
2f	Benzene–pet. ether	Yellow–red	53–54	254	75·6	7·1	11·0	75·4	6·9	11·3
4b	Benzene	Red	170	436	77·1	6·4	12·8	77·1	6·4	12·7
4d	Benzene–pet. ether	Red	52–53	386	74·6	6·7	14·5	74·8	6·6	14·6
4f	Benzene	Yellow (powder)	190	390	67·7	6·7	21·4	67·5	6·7	21·4
5b	Benzene	Red	201	555	75·7	5·95	12·6	75·7	5·8	12·4
5d	Benzene	Red	192–193	569	75·9	6·15	12·3	75·8	6·3	12·1
5f	Benzene	Red	210	589	71·25	5·4	11·9	71·6	5·4	11·5
5h	Benzene	Red	210	603	71·6	5·6	11·6	71·6	5·4	11·6

concentrated hydrochloric acid (1 ml). The solution was stirred for 40–50 h and was then heated to 40–45°C and maintained at this temperature for a further 4–5 h. The brownish-red solid which separated was filtered and dried. It was crystallised from petroleum ether to yield **3b** as reddish-yellow crystals (16·8 g, 60%), m.p. 111–112°C, IR (Nujol) ν (cm^{-1}): 3240, 1650. ^1H-NMR ($CDCl_3$) δ (ppm): 1·25 (6H, s, CH_3 of first benzene ring containing NH_2 group), 1·32 (6H, s, CH_3 of the other benzene ring), 2·8–3·2 (1H, m, CH of isopropyl group of first benzene ring), 3·8–4·2 (1H, m, CH of isopropyl group of other benzene ring), 4·0 (2H, s, NH_2, exchangeable with D_2O), and 6·8–8 (7H, m, aromatic protons). MS (*m/e*): 281 (M^+, 48%), 266 (61%), 224 (20%), 149 (78%), 133 (100%), 125 (22%), 119 (37%), 106 (52%), 91 (33%), 77 (9%).

Found: C, 76·7; H, 8·0; N, 14·9; $C_{18}H_{23}N_3$ requires: C, 76·9; H, 8·2, N, 14·9%.

3.3 General procedure for the synthesis of monoazo and disazo solvent dyes 2, 4 and 5

The appropriate arylamine (0·01 mol) was dissolved in a mixture of water (60 ml) and concentrated hydrochloric acid (10 ml) for **2**, or in a mixture of acetic acid (70 ml), water (30 ml) and concentrated hydrochloric acid for **4** and **5**. The solution was cooled to 0–5°C. A solution of sodium nitrite (0·01 mol) in water (20 ml) was added dropwise with stirring while maintaining the temperature at 0–5°C. After diazotisation was complete, excess nitrite was destroyed by addition of sulphamic acid. The diazo solution was then added dropwise to a cold alkaline solution of the naphthol coupling component (0·01 mol) maintaining a temperature of 0–5°C and a pH of 7–7·5. The azo dye which separated was filtered and washed with water. The crude dye was purified by column chromatography on silica gel using benzene/petroleum ether as eluent. Mass spectrometric, microanalytical and melting point data are summarised in Table 9.

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